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**Results of the Pilot-Scale
Treatability Study for the
Test Reactor Area Warm Waste Pond**

Volume I: Main Report

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R. A. Montgomery
R. A. Bessent
D. Gombert**



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No. DE-AC07-76ID01570*

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**Results of the Pilot-Scale Treatability Study for the
Test Reactor Area Warm Waste Pond**

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ABSTRACT

The use of physical separation/chemical treatment was selected as the preferred alternative, in the Interim Action Record of Decision (ROD) for the Warm Waste Pond (WWP) at the Test Reactor Area (TRA), to treat sediments in the WWP contaminated with chromium, cobalt-60 and cesium-137. Before this treatment alternative could be implemented, treatability studies were required to determine if the goals of the ROD could be met. The studies were performed at TCT-St. Louis and Westinghouse Idaho Nuclear Company, Inc. (WINCO), using samples collected by EG&G Idaho, Inc. Sample characterization included particle size distributions, radionuclide activity distributions, elemental distributions, Scanning Electron Micrograph analysis, and crystalline phase analysis of the samples. The Acid Extraction tests, performed at TCT, included extraction of sediment samples using nitric acid, treatment of the extraction liquids, and preliminary conceptual design. Treatment testing of the extraction liquids included precipitation, ion exchange, complexation/precipitation, and reverse osmosis. Selective Extraction tests, performed at WINCO to identify and attack the specific mechanisms of contamination in the sediment, included six sequential extractions of selected material phases in and on the sediment particles.

Radionuclide and chemical analyses were performed on the sediment, solid residues, and liquid extractants to determine the fates of cesium, cobalt, chromium, and many other species during the dissolution and treatment tests. Analyses were also performed for comparison to toxicity characteristic leaching procedure limits and Idaho Chemical Processing Plant Waste Acceptance Criteria.

At least 60 Wt.% of the sediment in the samples was in the +8 mesh size fraction. The larger sized particles have less contamination than smaller particles although none of the size fractions evaluated in these studies had cesium levels within the assumed ROD goal of 690 pCi/g for the average cesium level in sediment returned to the pond (occupational exposure scenario). Nitric Acid Extraction of the -8 mesh sediment, using up to two Acid Extraction stages, removed up to 91% of the cesium, but cesium activity in the treated sediment still exceeded the 690 pCi/g goal. Removal of chromium and cobalt from the extraction liquids by complexation/precipitation was quite effective, but the technologies tested were less successful in removing cesium.

The sequential extractions verify that significant recovery of cobalt and chromium species can be achieved with chemistries less aggressive than hot nitric acid. Sequential extractions can also provide an accurate account of contaminant distribution in the sediment phases. About 84% of the cobalt is associated with phases in and on sediment particle coatings that can be removed by soil washing techniques less harsh than nitric acid. About 67% of the cobalt is associated with the easily reducible manganese oxide phase. For chromium, about 93% is associated with phases in and on sediment particle coatings that can be removed by soil washing techniques. About 57% of the chromium is associated with the moderately reducible iron oxide phase. Only 18% of the cesium is associated with phases in and on sediment particle coatings that can be removed by soil washing techniques less harsh than nitric acid. About 82% of the cesium is associated with the sediment particle lattice structure and can be removed only by partial or complete dissolution of the sediment particles.

From a preliminary conceptual design of a combined physical separation and chemical treatment process for the sediment, estimated total costs are much higher than the \$7.2 million cost estimated

in the ROD. In addition, the assumed goal in the ROD of less than 690 pCi/g for the average cesium activity for sediment returned to the pond cannot be met, unless (a) significant amounts of sediment are not returned to the pond or (b) the averaging effect of clean covering soil is included with the returned sediment.

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ACRONYMS

ASTM	American Society for Testing and Materials
ATR	Advanced Test Reactor
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
CLP	Contract Laboratory Program
COCA	Consent Order and Compliance Agreement
DOE	U.S. Department of Energy
DOT	U.S. Department of Transportation
DRR	Document Revision Request
EG&G Idaho	EG&G Idaho, Inc.
EDS	electron dispersive spectroscopy
EPA	Environmental Protection Agency
ERD	Environmental Restoration Department
ERP	Environmental Restoration Program
ICP	inductively coupled plasma
ICPP	Idaho Chemical Processing Plant
IDHW	Idaho Department of Health and Welfare
INEL	Idaho National Engineering Laboratory
NCP	National Contingency Plan
NPL	National Priorities List
PFD	process flow diagram
QA/QC	Quality Assurance/Quality Control
RCRA	Resource Conservation and Recovery Act
RI/FS	Remedial Action/Feasibility Study
RO	Reverse osmosis
ROD	Record of Decision
SEM	scanning electron micrograph
SOP	standard operating procedure
TCLP	toxicity characterization leaching procedure
TRA	Test Reactor Area
WAC	Waste Acceptance Criteria
WAG	Waste Area Group
WINCO	Westinghouse Idaho Nuclear Company
Wt. %	weight percent
WWP	Warm Waste Pond

Results of the Pilot-Scale Treatability Study for the Test Reactor Area Warm Waste Pond

1. INTRODUCTION

The Warm Waste Pond (WWP) system at the Test Reactor Area (TRA) of the Idaho National Engineering Laboratory (INEL) consists of three interconnecting cells. The cells are unlined, and the sediment in the cells contains various levels of contaminants from wastewater discharged from TRA facilities since 1952. The pond was designed to receive slightly radioactive (warm) wastewater but, prior to 1962, all liquid waste except sanitary sewage was discharged to the pond (Doornbos et al. 1991 and Hull 1989). Warm wastewater is first discharged to an underground, enclosed retention basin, where residence time is sufficient for the effective decay of short-lived radionuclides. After decay of short-lived radionuclides, the wastewater is discharged to the pond. The pond is fenced and is under institutional control.

The amount of warm wastewater discharged to the pond has significantly decreased since the 1970s. Quarterly discharge rates decreased from over 60 million gal in 1974 to around 5 million gal in 1983. Also, beginning in 1983, the warm wastewater is treated to remove dissolved and suspended radioactive isotopes at the TRA Warm Waste Treatment Facility. Warm wastewater from the Advanced Test Reactor (ATR) is similarly treated at the ATR Warm Waste Treatment Facility. A new, lined evaporation pond was constructed in 1992 and will be placed into used in 1993. All water discharges to the present percolation pond will then be halted. Use of the new evaporation pond will prevent future contamination of the environment with metals or radionuclides.

1.1 Background

The INEL was listed on the National Priorities List (NPL) of the National Contingency Plan (NCP) by the U.S. Environmental Protection Agency (EPA). Since then, the U.S. Department of Energy (DOE), EPA, and the State of Idaho determined that the WWP should be remediated in accordance with the Comprehensive Environmental Response, Compensation and Liability Act of 1980 (CERCLA) process, as implemented by the Federal Facilities Agreement/Compliance Order. The CERCLA process includes a Remedial Investigation/Feasibility Study (RI/FS). The Phase I RI/FS Work Plan (Van Deusen and Trout 1990) was submitted to the EPA and the State of Idaho in April 1990 (Doornbos et al. 1991). This work plan described additional studies required before remedial action decisions could be made.

In December 1991, an Interim Action Record of Decision (ROD) (DOE 1991) addressed the most significant potential risks of the pond, and identified the selected remedy to reduce these risks. The most significant risks are external exposure to radiation, and inhalation and/or ingestion of contaminated sediment. The key risk-driver, identified by the risk assessment and addressed in the ROD, is the radionuclide cesium-137. The ROD also identifies as important contaminants cobalt-60 and nonradioactive chromium. The selected treatment process was a combination of physical and chemical removal of contaminants from the sediment. Placement of an interim soil cover, followed by further investigation, is a ROD option should physical or chemical treatment fail to meet ROD criteria and assumptions.

There are a number of organic, inorganic, and radiological contaminants in the pond sediment. Both present and future human health risks from these contaminants were evaluated in the ROD. Risks were determined for individual contaminants, combined contaminants, and multiple exposure

pathways for radionuclides. Noncarcinogenic and carcinogenic effects were both evaluated. According to this risk evaluation, the levels of most of the contaminants present in the sediment are within acceptable NCP target risk ranges. However, the present carcinogenic risks from the external exposure pathway for radionuclides exceeded the NCP target risk range. Cesium-137 and cobalt-60 were the risk drivers because of their relatively high concentrations. For future scenarios (a residential family receptor, residing at the site starting in 100 years), the carcinogenic risk due to combined inhalation and ingestion exceeded the NCP target risk range. Cesium-137 was the primary risk driver in this future risk evaluation.

Although sediment samples have passed Toxicity Characteristic Leaching Procedure (TCLP) tests for metals and organics (Doornbos et al. 1991), the reduction of the chromium levels in the pond was also specified in the ROD. Significant amounts of hexavalent chromium in cooling water have been discharged to the pond in earlier years. During the ensuing years to present, essentially all of the hexavalent chromium has been reduced to the relatively innocuous trivalent form of chromium (Doornbos et al. 1991).

Treatment goals assumed in the ROD are (a) a 60% total sediment volume reduction by screening, (b) 90% removal of combined cesium, cobalt, and chromium, and (c) reduction of the average cesium level to 690 pCi/g for all sediment returned to the pond. The use of physical separation and chemical extraction of the TRA WWP sediment has been identified in the ROD as the selected treatment alternative. Preliminary bench-scale tests, upon which the ROD was based, have shown the potential of these types of processes to reduce contamination in the sediment (Beller and Bessant 1991). The bench-scale tests indicated that about 60 Wt.% of the sediment was larger-sized sediment particles (larger than about 8 mesh), and the remaining 40 Wt.% was smaller-sized sediment particles less than about 8 mesh. The larger particles were less contaminated with cesium, cobalt, and chromium than were the smaller particles. Levels of these contaminants in the sediment could be reduced through dissolution in strong mineral acids. The most effective acids were hydrochloric and nitric acids, in that order. After dissolution, the extract containing the dissolved contaminants is an undesirable secondary waste stream. Levels of chromium and cobalt in the solution could be reduced through precipitation as the hydroxide or through ion exchange. However, all attempts to isolate the cesium proved unsuccessful. Methods attempted included ion exchange and selective membrane filtration.

The bench-scale testing indicated that dissolution by strong mineral acids results in some undesirable process implications:

- A secondary waste stream is generated consisting of the acid extract containing dissolved, concentrated contaminants.
- Additional process steps are necessary to remove the dissolved contaminants to reduce the volume of secondary wastes.
- Measurable dissolution (about 8.5%) of the sediment particles adds to the amount of secondary wastes and complicates the removal of the dissolved contaminants by forming sludges upon pH adjustment of the acid extract. These sludges would require a significant waste management effort at considerable cost.
- Acid dissolution works best with higher concentration acids at elevated temperatures, complicating system design, operation, and personnel safety.

- The Idaho Chemical Processing Plant (ICPP) Waste Acceptance Criteria (WAC) severely limits the concentration of chlorides in the waste solution. The most acceptable process for solidifying the secondary extractant liquids is calcination at the ICPP. However, this eliminates the use of hydrochloric acid for contaminant extractions and requires the use of the slightly less effective nitric acid.

These implications must be resolved before implementation of the physical screening and chemical extraction remedy selected in the ROD. A treatability study was designed to address these implications. The treatability study includes field sample collection and laboratory tests and analyses to evaluate physical separation and chemical extraction of the sediment. The field sample collection was performed in accordance with the field sampling plan (Blackmore 1992 and Salomon^a) and the quality assurance project plan (Flynn 1992). The field sample collection is briefly described in Section 2.1. The laboratory tests and analyses were conducted in accordance with the work plan (Montgomery et al. 1992).

1.2 Objectives of the Work Plan

The overall objectives of this study are specified in the work plan (Montgomery 1992) as follows:

- **Acid Extraction**—Determine the best combination of nitric acid concentration, temperature, and leach times to remove chromium, cobalt, and cesium in quantities sufficient to meet the risk-based criteria established in the ROD
- **Selective Extraction**—Determine if there exists any method, short of dissolution in hot, strong mineral acid, that will selectively remove chromium, cobalt, and cesium from pond sediments. Such a method might prove substantially easier and safer, producing a lower volume of final waste product by determining the controlling fixation mechanism(s) for chromium, cobalt, and cesium in the WWP sediment. The contaminants may then be selectively extracted by attacking the controlling fixation mechanisms.

The Acid Extraction evaluation was performed by TCT-St. Louis under contract to EG&G Idaho, Inc. (EG&G Idaho). Several subordinate objectives for their evaluation were as follows; with the phase(s) of the test program in parentheses where ever objective is addressed:

- Determine chemical compatibility with the ICPP WAC and any other possible waste storage/disposal options, such as solidification. Chemical testing will determine if wastes classified as hazardous under the RCRA, are generated during the treatment process and how they might be handled to meet any applicable or relevant requirements (Phases B, C, and D).
- Develop data that will allow estimates of raw materials and plant scale necessary to achieve remediation of pond sediments (Phase C).
- Determine average leach rates for chromium, cobalt, and cesium, using 2 kg samples of sediments, in nitric acid, under optimum conditions (Phase C).

a. Personal communication from Salomon (EG&G Idaho, Inc.) to R. A. Montgomery (EG&G Idaho, Inc.), August 1992.

- Identify critical physical and chemical parameters having major effects on technology performance (Phase B and WINCO).
- Determine a mass balance for chemical and substrate fate at all stages of the extraction and subsequent treatment (Phases B and C, and WINCO).
- Determine the estimated cost of soil washing based upon quantities of chemicals used in the test (Phase C).
- Based upon results of the screening tests, develop candidate treatment trains (scenarios) that have the ability to meet risk-based cleanup levels (Phase A).
- Based upon the results of the evaluations, identify the optimal treatment scenario that has the ability to meet risk-based cleanup levels from the sediment matrix (Phase B).
- Using data generated from the treatability studies, generate preliminary design criteria for candidate treatment technologies that have the ability to meet risk-based cleanup levels (Phase C).
- Further explore, through the treatability screening process, candidate technologies for the removal and subsequent concentration of cesium from extraction fluids (Phase D).

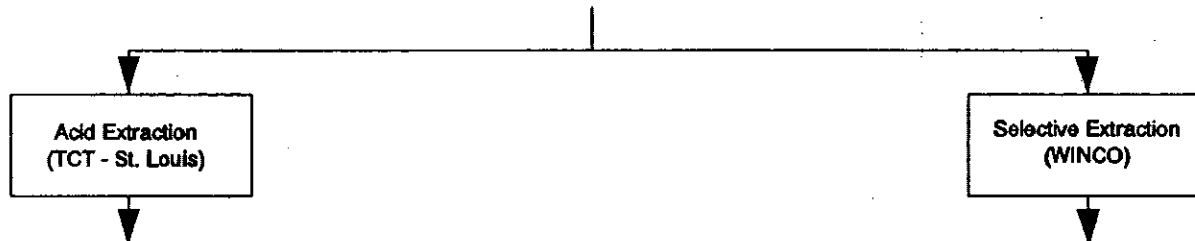
The Selective Extraction evaluation was performed at the INEL by the Westinghouse Idaho Nuclear Company, Inc. (WINCO). Subordinate objectives of the Selective Extraction evaluation were as follows:

- Verify the experimental technique of sequential extraction for selectively attacking the fixation mechanisms to provide a basis for evaluating soil washing.
- Determine the optimum extent of decontamination achievable as a function of soil matrix dissolved. These data are to be compared to Acid Extraction, demonstrated to remove 80+ % of the cesium contamination while dissolving 8+ % of the soil matrix.
- Determine the amount of contamination held in the mineral matrix, which represents the absolute limiting values for practical application of soil washing.
- Pending results from tests above, develop guidance for designing a flowsheet targeting the primary fixation mechanism(s) to optimize the performance of sediment washing.
- Develop recommendations on the applicability of Selective Extraction technology to the contaminants in the WWP soils.

1.3 Scope of Work

The scope of work for the treatability study is summarized in Figure 1-1. This scope of work was defined to satisfy the overall project objectives listed in Section 1.2. Details of the Acid Extraction scope of work performed by TCT-St. Louis are provided in Section 1.3.1. Details of the Selective Extraction scope of work are provided in Section 1.3.2.

Sediment Samples



Phase A - Evaluate physical separation, particle size distribution, and contaminant

Phase B - Parametric and staged nitric acid extraction

Phase C - Optimal nitric acid extraction and precipitation, and ICPP acceptability

Phase D - Treatment of extractant solution and ICPP acceptability

- Initial sediment characterization
 - Particle size distribution
 - Radionuclide distribution
 - Elemental distribution
 - SEM characterization
 - Major crystalline phases
 - Size separation
- Time release profiles
- Sequential selective extractions
 - Ion exchange phase
 - Carbonate phase
 - Easily reducible metal oxides phase
 - Moderately reducible refractory metal oxides phase
 - Organic phase
 - Crystal lattice (matrix)

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Figure 1-1. Treatability study scope of work.

1.3.1 Acid Extraction

The Acid Extraction study was performed in Phases A-D in accordance with the work plan. In Phase A, the sediment samples were characterized for (a) particle size distribution and (b) radiological and metals (total and TCLP) contaminant levels by particle size. The Phase A tests were also performed to evaluate physical size separation of the sediment to reduce volume of the more contaminated material and to generate the samples for the Phase B chemical extraction tests.

The Phase B tests included a parametric evaluation of nitric Acid Extraction under various selected time, temperature, and acid concentration conditions. The results of the Phase A tests verified that at least 60% of the mass of the sediments was +8 mesh. Therefore, the remaining 40% or less of the sediment samples from Phase A was evaluated by chemical extraction in Phase B. Prior to the beginning of the Phase B tests, this approach was mutually agreed to by the U.S. Department of Energy (DOE), EPA, and the Idaho Department of Health and Welfare (IDHW).

Based on the parametric tests, the optimum conditions were selected for a second staged extraction of sediment, to evaluate the potential for staged extraction. The extractant solution from optimum extraction conditions was analyzed for metals content and activity to determine acceptability according to ICPP WAC.

In Phase C, larger samples were used to verify Acid Extraction performance under the optimum conditions defined in Phase B. The extractant solution from optimum extraction conditions was analyzed for metals content and activity to determine acceptability according to ICPP WAC. The extracted sediment was analyzed to determine the feasibility of returning extracted sediment to the WWP. Precipitation of the dissolved sediment and contaminants was evaluated by pH adjustment, and the supernatant from the precipitation step was again analyzed for ICPP WAC acceptability.

The Phase D tests were performed to evaluate the treatment options for the extractant solution. Removal of cesium, cobalt, and chromium by ion exchange, precipitation/complexation, and membrane filters was evaluated. The treated solutions were analyzed for ICPP WAC acceptability.

Also included is an evaluation of preliminary design, performance, and costs for treatment train scenarios.

1.3.2 Selective Extraction

The experimental plan followed the work plan and was designed at the laboratory screening level in accordance with the EPA guidance documents for conducting treatability studies (Pheiffer et al. 1990 and EPA 1989) in support of the remedy selection process under the CERCLA. Sediment samples were physically and chemically characterized, and contaminant distribution data was analyzed to determine if there were any correlations between contaminants and soil matrix characteristics. Sequential extractions were then conducted to accomplish the following goals:

1. Determine the controlling fixation mechanism(s) for chromium, cobalt, and cesium in the WWP sediment.
2. Verify the experimental technique of sequential extraction for selectively attacking fixation mechanisms to provide a basis for evaluating physical separation/chemical extraction

3. Determine qualitatively the maximum extent of decontamination achievable by comparing contaminant release to the extent of soil matrix dissolved. This data is to be compared to Acid Extraction reported to remove up to 80% of the cesium contamination while dissolving around 8% of the -8 mesh soil matrix.
4. Determine the amount of contamination held in the mineral matrix, which represents the absolute limiting values for practical application of soil washing.
5. Pending results from 3 and 4 above, develop guidance for designing a flowsheet targeted on the primary fixation mechanism(s) to optimize the performance of soil washing.
6. Develop recommendations on the applicability of soil washing technology to the contaminants in the WWP soils.

1.4 Project Organization and Responsibilities

This project was conducted by DOE. The field sample collection and handling was performed by EG&G Idaho. The Acid Extraction testing laboratory analysis was performed by TCT-St. Louis, and the Selective Extraction testing and laboratory analysis was performed by WINCO. A portion of the Acid Extraction sample analysis (the gamma spectroscopy) was subcontracted by TCT-St. Louis to Core Laboratories in Casper, Wyoming. The organization of the treatability test program is shown in Figure 1-2.

1.5 Guide to Report

This report is presented in two volumes. In "Volume I: Main Report," the treatability study is summarized. This summary includes an abstract and sections that present the introduction, sample collection and test procedures, sediment characterization, results of the acid extraction tests, results of the selective extraction tests, and conclusions. Volume I includes one attachment (Attachment A) that presents the response to EPA and IDHW comments. These comments were made on the draft version of this report dated January 1993. Volume I can be essentially a stand-alone document, but it does not include all of the detailed information that is found in "Volume II: Appendices."

The contents of Volume II include the reports presented to EG&G Idaho from the subcontractors, TCT-St. Louis and WINCO. For completeness, the same abstract and table of contents for both volumes that appear in Volume I are repeated in Volume II. The acid extraction testing was performed by TCT-St. Louis and is detailed in their report (Appendix A in Volume II). The selective extraction tests were performed by WINCO and are presented in the WINCO report (Appendix B of Volume II). The TCT report includes Attachments A-M, while the WINCO report includes Attachments A and B.

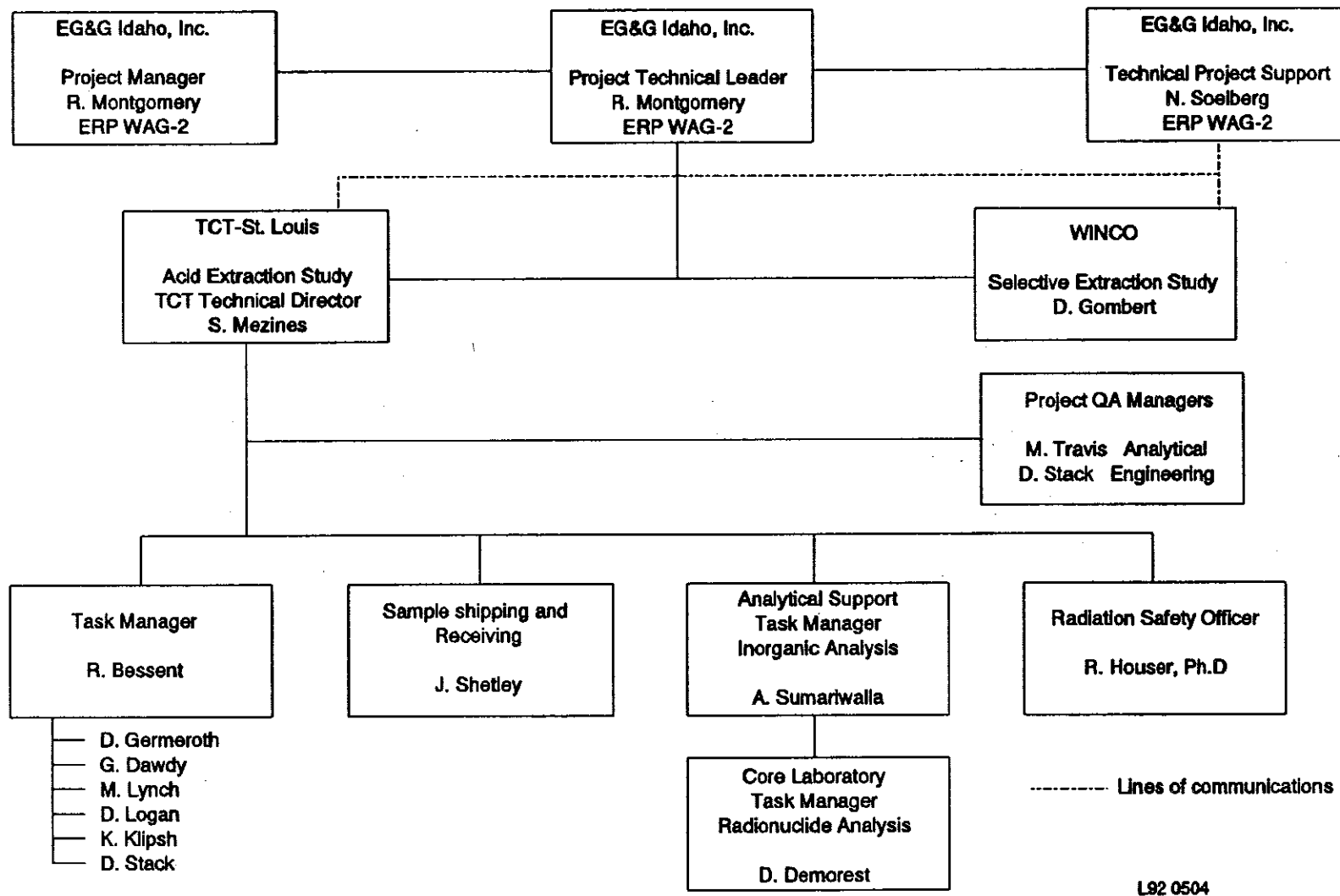


Figure 1-2. Treatability study organization and responsibilities.

2. SAMPLE COLLECTION, TEST PROCEDURES, AND ANALYSES

This treatability study included laboratory testing and analysis of selected sediment samples. Sediment samples were collected from specified pond locations in August 1992 for the Acid Extraction (by TCT-St. Louis) and the Selective Extraction (by WINCO) test programs.

2.1 Field Sample Collection

Sample collection at the ponds was performed by EG&G Idaho personnel according to the field sampling plan (Blackmore 1992 and Salomon^b), the quality assurance project plan (Flynn 1992), and the health and safety plan (Blackmore and Peterson 1992). There were only three minor variations to the field sampling plan, which were made to obtain better samples and sample documentation. These minor variations do not compromise the quality of the sample collection. The variations are briefly described below.

A total of 15 samples were collected and placed in U.S. Department of Transportation (DOT) Type-7A cans. The average weight per can was about 25 lb. The locations where these samples were collected are shown in Figure 2-1. Some of the samples were collected from areas of average pond sediment cesium activity of around 9,960–11,500 pCi/g, based on prior test results (Blackmore 1992 and Montgomery et al. 1992). Three samples each were collected from locations G, L, K, and N. Three other samples were collected from an area that had cesium activity near the maximum cesium levels, which exceed 39,000 pCi/g. These high cesium-activity samples were collected from location Z. In accordance with the field sampling plan, location Z was identified as the sample location for the high cesium-activity samples from its high radiation field. Radiation field measurements were as high as 250 mR/hr at this location. The samples were grab samples, collected to a depth of 4–6 in. in the sediment by a shovel.

There were three variations in the performance of sampling program compared to the field sampling plan. Two of these variations were documented in field Document Revision Requests (DRRs). The first DRR was a change in the sample type designation number in the identification codes for the samples, to make the sample identification numbers more consistent with the sample descriptions. The second DRR change was corrections of the coordinates for two of the sample locations identified in the sampling plan, changing south to north and northwest to northeast. The third variation was not included in a DRR. This change was the use of DOT Type 7A cans for shipping rather than Type 7C cans as specified in the field sampling plan. Type 7A cans are the appropriate containers for shipping these types of radioactive samples.

2.2 Laboratory Test Procedures and Analyses

The test and analytical procedures for both the Acid Extraction and Selective Extraction programs were performed according to the treatability study work plan (Montgomery 1992). The laboratories also complied with the quality assurance plans and activities specified in the work plan for TCT and WINCO.

b. Personal communication from H. Salomon (EG&G Idaho, Inc.) to R. A. Montgomery (EG&G Idaho, Inc.), August 1992.

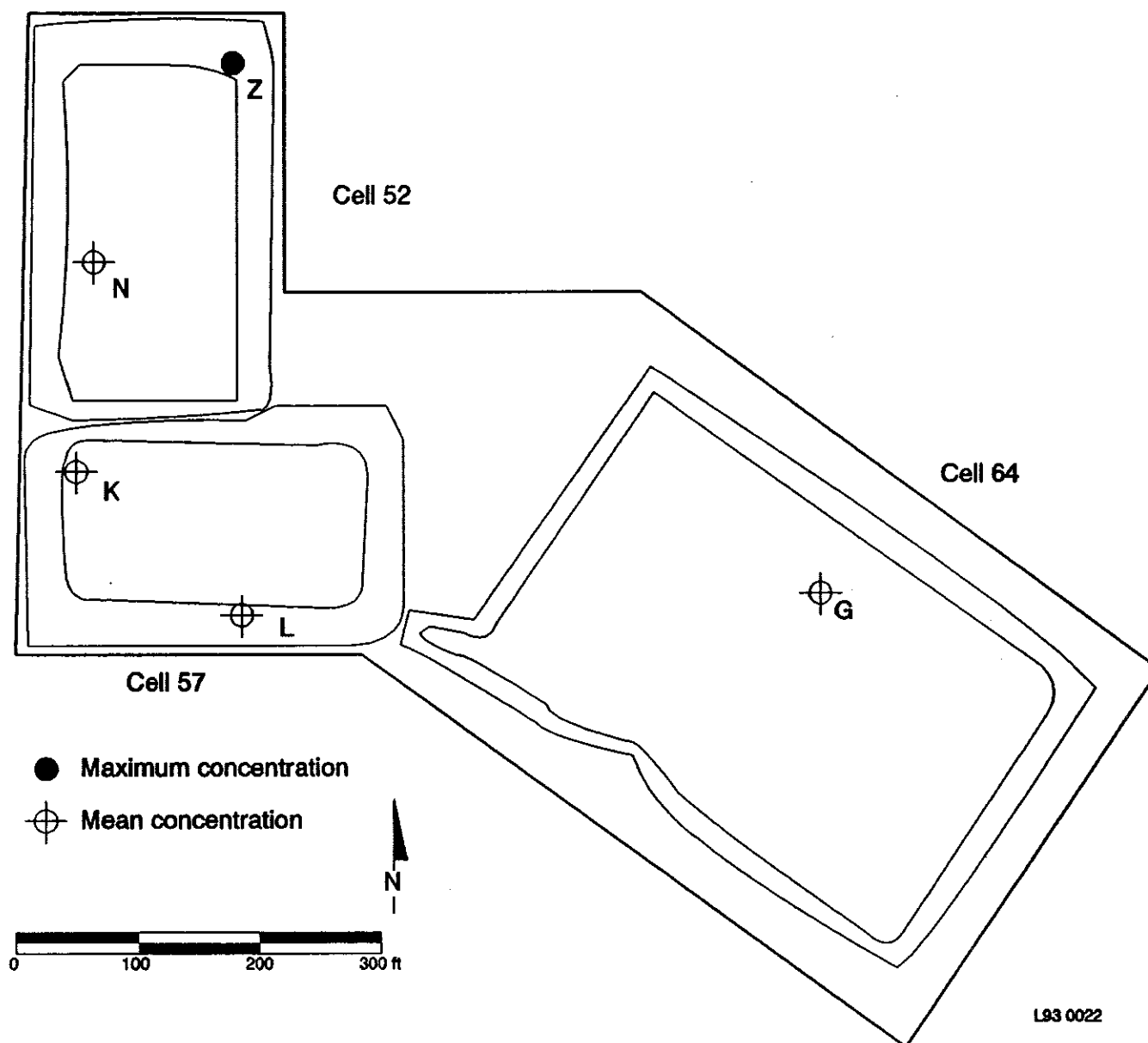


Figure 2-1. WWP sample locations.

There were many different analytical procedures used in the Acid Extraction and Selective Extraction programs. Analytical procedures used during the Acid Extraction program by TCT are summarized in Table 2-1. Analytical procedures used in the Selective Extraction program by WINCO are summarized in Table 2-2. Some of these procedures identified in Tables 2-1 and 2-2 are different from those specified in the work plan. The revised procedures are equivalent to or superior to those specified in the work plan.

During the performance of the laboratory treatability studies, there were a few slight deviations and additions to the procedures and activities specified in the work plan. In Sections 2.2.1 and 2.2.2, the test procedures are summarized, and minor deviations to the work plan are identified. These minor deviations were implemented due to new information not available at the time the test plan was prepared, or to obtain more complete or improved test results. These deviations do not compromise the quality of the test results.

2.2.1 Acid Extraction Tests and Analyses

The Acid Extraction testing was performed on sediment samples of two different cesium activity levels. Some of the samples contained cesium activity levels representative of the average pond sediment cesium activity of around 9,690–11,500 pCi/g (Blackmore 1992 and Montgomery et al. 1992). The cesium concentration was chosen as the primary indicator because the bench scale treatability studies indicated that cesium is significantly more difficult to remove from ponds sediments than chromium or cobalt. Additionally, cesium proves more intractable to final isolation and treatment than either chromium or cobalt. Cesium is also identified as the primary risk-driver in the ROD. Thus, if the cesium can be successfully removed and treated, then both chromium and cobalt are expected to also be satisfactorily treated. To confirm this assumption, chromium, cesium, and cobalt concentrations were measured at all steps through the processes.

Upon receipt of sediment samples at the TCT shipping and receiving department, the samples were concurrently logged into the laboratory system and into the treatability sample logbook that was used during the treatability activities. The samples were also screened for radioactivity using a geiger counter. All of the procedures associated with the receipt of radioactive waste samples were performed in accordance to the TCT Radiation Safety Plan presented in Appendix A.

All of the physical and chemical test procedures were performed at TCT. The gamma spectroscopy analysis for radionuclide activity was performed at Core Laboratories in Casper, Wyoming, under contract to TCT. All other analyses were performed at the TCT Laboratory.

The Acid Extraction program was performed in a series of Phases A–D, according to the test plan. The objectives of each of the phases are summarized in Section 1.3. Standard test conditions and operating conditions are summarized in Table 2-3.

Procedures specific to each of the Phases A–D are summarized as follows:

Phase A:

The design of the Phase A testing is shown in Figure 2-2. These tests were performed in duplicate. Sieving was performed on at least 5 kg of sediment material per test. Particle sizing was performed per American Society for Testing and Materials (ASTM) D 421 (1985).

Table 2-1. Summary of analytical methods used during WWP sediment pilot study.

Analyte	EPA method number
Arsenic	200.7
Barium	200.7
Cadmium	200.7
Chromium	200.7
Lead	200.7
Mercury	245.1
Nickel	200.7 [Inductively coupled plasma (ICP)]
Potassium	258.1
Selenium	200.7 (ICP)
Silver	200.7 (ICP)
Sodium	200.7 (ICP)
Zinc	200.7 (ICP)
Total cyanide	9010
Loss on drying (LOD)	160.3
Chloride	325.2
Fluoride	340.2
Sulfate	375.2
Phosphate	365.4
Total organic carbon (TOC)	9060
Total suspended solids (TSS)	160.2
Gross beta	9310
Gamma spec (cesium-137, cobalt-60, iodine-131)	901.01
Isotopic uranium (uranium-234, uranium-235, uranium-238)	908.0
Plutonium- 238 and 239	907.0
Total plutonium	907.0

Table 2-2. Summary of analytical methods used during Selective Extraction study.

Analyte	Technique	WINCO Analytical method #	Standard method
Chromium	ICP	2900	SW-846; 6010A
Silicon	ICP	2900	—
Aluminum	ICP	2900	SW-846; 6010A
Manganese	ICP	2900	SW-846; 6010A
Iron	ICP	2900	SW-846; 6010A
Calcium	ICP	2900	SW-846; 6010A
Sodium	AA ^b	2119	SW-846; 7770
Potassium	AA	2119	SW-846; 7610
Cesium-137 Cobalt-60	Gamma ^c scan	3993	—
NO ₃	IC ^d	8104	9056; EPA-600 Method 300
Alternative NO ₃ ⁻ -NH ₄	—	7071	Kjeldahl titration method
Chlorine	IC	8102	9056; EPA-600 method 300
Inorganic carbon	—	8062	ASTM D4129-82
Total carbon	—	8061	ASTM D513-82

a. Inductively coupled plasma spectroscopy.

b. Atomic absorption spectroscopy.

c. Gamma spectroscopy.

d. Ion chromatography.

Table 2-3. Summary of standard test conditions and/or procedures for Acid Extraction tests.

1. All treatability testing was performing in the TCT treatability laboratory at room temperature or as specified by specific test procedures.
2. All treatability testing was performed at ambient pressure.
3. Treatability sampling was performed in accordance with standard sampling protocol that generates a representative sample for chemical and/or physical analysis. For screening and pilot studies, the sample volumes generated were relatively small. Therefore, in most cases, an entire treated sample, or extractant, was transferred directly from the testing apparatus to the appropriate sample container for the parameter to be analyzed. In some cases, a small stainless steel spatula was used to collect solid samples associated with treatability activities.
4. All treatability activities were performed in accordance with TCT laboratory and radiation safety requirements.
5. Shipments of environmental samples to Core Laboratories or EG&G Idaho were performed in accordance with appropriate DOT and radiation safety procedures.
6. All treatability activities were documented in logbooks maintained by the engineers and technicians evaluating treatment technologies.
7. The glassware used in the treatability activities were cleaned and "prepped" using the "TCT-St. Louis Standard Operating Procedure (SOP) for Bottle Preparation," which eliminated "cross-contamination" between tests.
8. As indicated in the treatability study test plan, some of the techniques used during treatability studies are considered imprecise. In addition, some of the initial results in early phases of the treatability study provided information that suggested or indicated that minor changes in the subsequent test design was warranted to improve the quality of test results. Flexibility for making changes and the mechanism by which changes were made was specified in the treatability study test plan. The mechanism included review and approval by EG&G Idaho prior to implementation of change, in accordance with Environmental Restoration Program (ERP) Directive 4.1. Any changes that were made are summarized in this report.
9. Where applicable, TCT photo-documented treatability activities.
10. Analytical Quality Level I was used to qualitatively screen samples generated from treatability screening tests for indicator constituents. Level I basically provided an indication of the presence of a contaminant in a sample with limited quality assurance/quality control (QA/QC) requirements. Level I analyses performed during treatability tests included primarily geiger counter monitoring. The methods associated with screening tests performed are described in subsequent sections of this report.

Table 2-3. (continued).

11. Analytical Quality Level III was used to quantitatively identify the concentration of contaminants of concern in samples generated from pilot-scale treatability activities. The detection limits associated with Analytical Level III was similar to Contract Laboratory Program (CLP) protocol and also required a rigorous QA/QC. The parameters analyzed using Level III protocol included the radionuclides, total metals, TCLP metals, and percent solids listed in Table 2-1.
 12. The performance of the specific technologies evaluated during treatability activities reflected the concentrations of contaminants of concern present in the original WWP sediment samples submitted to TCT by EG&G Idaho.
-

Samples of sieve sizes +4 mesh, 8 to 4 mesh, 16 to 8 mesh, 50 to 16 mesh, 100 to 50 mesh, 200 to 100 mesh, and < 200 mesh were analyzed for TCLP metals, total metals and gamma spectrum parameters. Samples of the +4 mesh sediment material were analyzed for total metals and gamma spectrum parameters. The sediment material associated with each of the six sieve size ranges was initially thoroughly mixed with a spatula or stainless steel spoon to create a relatively homogenous sample for analysis. After the mixing was completed, approximately 25–50 g of the sample was transferred, with a clean spatula, spoon, or scoop, into a 4-ounce glass bottle for shipment to Core Laboratories for gamma spectrum analyses. In addition, approximately 100–125 g of the mixed sample was transferred to another 250-mL amber glass bottle for total and TCLP metals analyses by the TCT laboratory.

Shipment of radioactive sediment and extractant samples to Core Laboratories was performed in accordance to appropriate DOT regulations and using guidance provided by the TCT and Core Laboratories radiation management and safety programs. Approximately 10% of all of the samples shipped to Core Laboratories for radionuclide analyses were blind duplicates used to check radionuclide data quality.

There were no deviations from the work plan or additions performed during this phase.

Phase B:

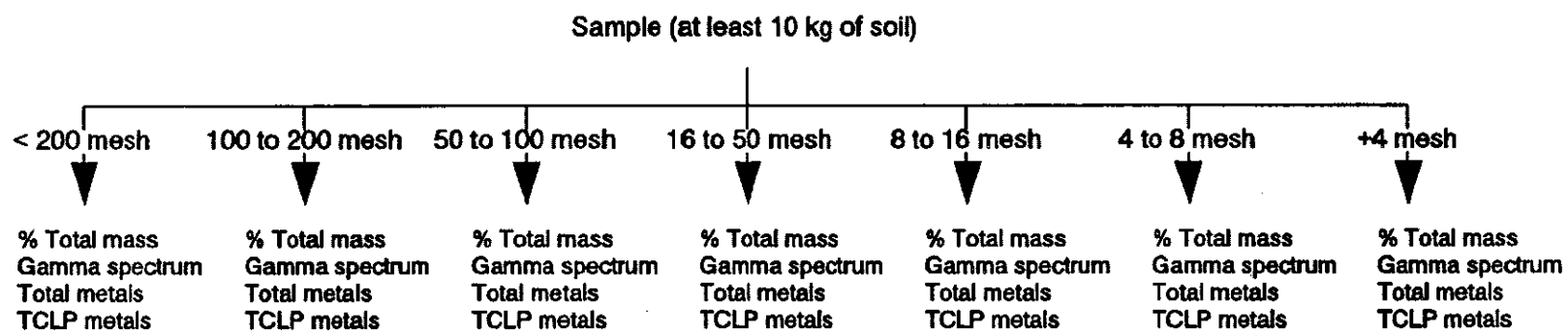
The flowsheet for the Phase B tests is shown in Figure 2-3. There were approximately 54 tests (including duplicates) performed during Phase B treatability activities. The parametric extraction tests were performed in glass beakers in which the acid solution and the sediment were heated and continuously mixed. Following each extraction test, the solid residue was centrifuged and filtered from the extractant liquid. The residues were dried and weighed before any analyses were performed.

Following the extraction tests, the optimum extraction condition was selected with the concurrence of DOE, EPA and IDHW, for more detailed analysis of the liquid and solid residue phases. This optimum condition used 3 M nitric acid at 95°C for 8 hours. A second extraction was also performed at the optimum condition on the residue from the first extraction at optimum condition to evaluate the potential of staged extraction.

Soil samples contain average Cesium-137 level

Perform duplicate sieving and analyses

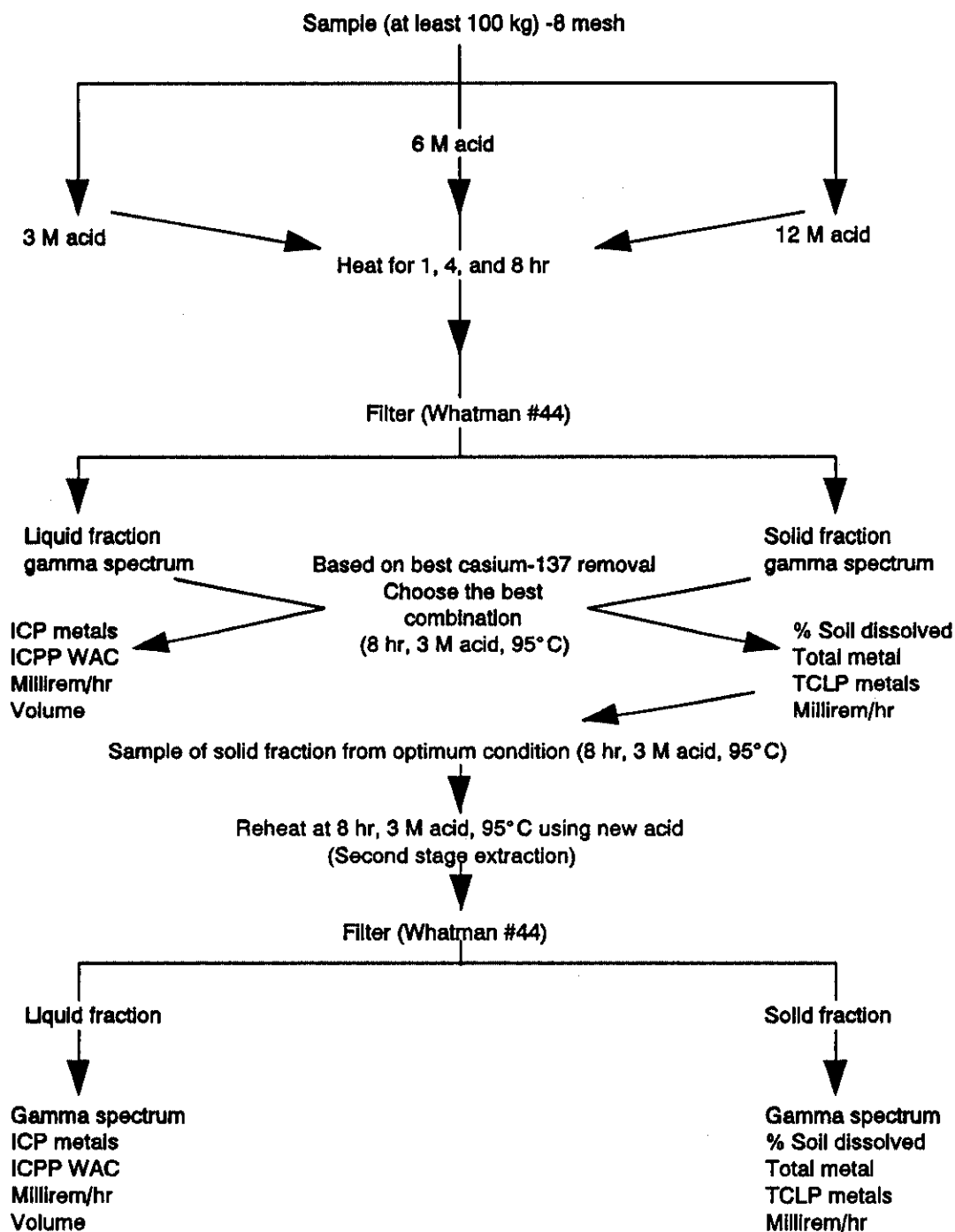
Use 4, 8, 16, 50, 100, and 200 mesh screens



L92 0499

Figure 2-2. Acid extraction Phase A flowsheet.

Dissolution performed at 50, 70, and 95°C
 Duplicate samples
 4 L nitric acid solution/kg soil



L92 0502

Figure 2-3. Acid extraction Phase B flowsheet.

The extracted sediment generated during Phase B tests was removed by centrifuging at 2,500 rpm for 10 minutes and filtering the supernatant. Extractant resulting from the Acid Extraction tests was subsequently poured into sample bottles, and preserved as needed, before analysis by Core or TCT laboratories.

There were no deviations from the work plan or additions performed during this phase.

Phase C:

The flowsheet for the Phase C tests is shown in Figure 2-4. The Phase C testing was performed in duplicate using sediment material having average cesium concentration and also sediment material having cesium-137 concentrations approaching maximum concentration. Larger samples of approximately 2 kg of -8 mesh material each were extracted using the optimum conditions determined in Phase B. The extractant was separated from the solid residues. After volumetric determinations, a portion of the extractant was pH adjusted to a pH of 9.0 for evaluation of precipitation. Following centrifuging and filtration, the extractant samples were analyzed for activity, metals, and ICPP WAC.

There were two additions to the activities specified in the work plan for this phase:

- The solid extracted residues were rinsed with distilled water following the filtration step to reduce the potential of residual acid containing dissolved contaminants in the residues.
- The solid extracted residues for some representative samples were sieved using 16 mesh, 50 mesh, and 200 mesh screens and separately analyzed for cesium and cobalt. This was added to the scope in order to evaluate the extraction effectiveness and the remaining activity for different sized particles.

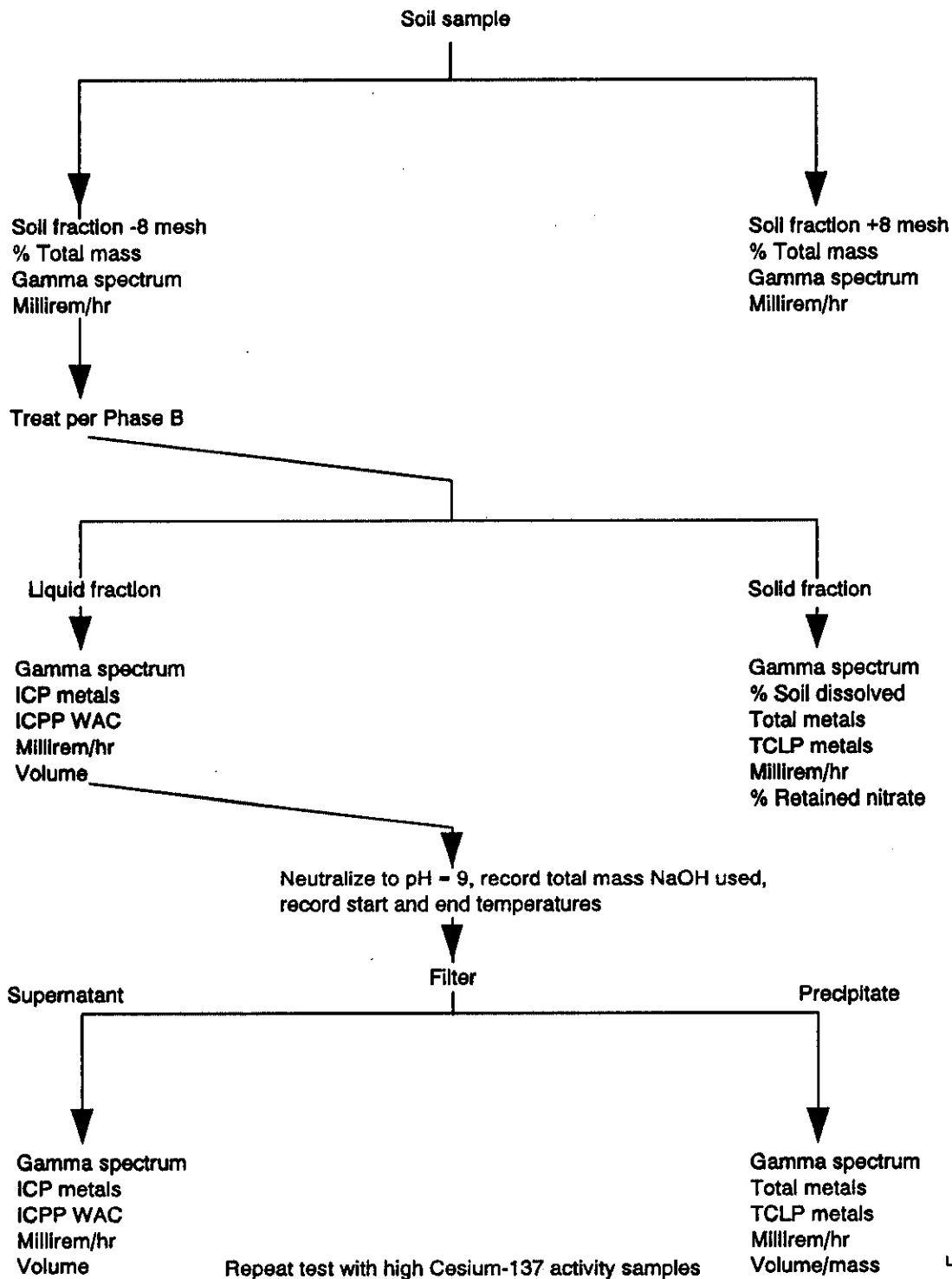
Phase D:

The flowsheet for the Phase D tests is shown in Figure 2-5. The evaluation of three different treatment/concentration technologies during Phase D activities dictated the need for three specific experimental procedures. This section addresses the three different experimental procedures used during the performance of ion exchange, precipitation/complexation, and membrane filtration tests.

Ion exchange tests were conducted using three ion exchange resins that have been documented to concentrate cesium and cobalt contained in liquid waste streams. The procedures outlined in the publication *Rohm and Haas Ion Exchange Resins; Laboratory Guide* (Rohm and Haas 1988) were used as a guide to establish ion exchange resin dosage, solution pH and contact time using batch methodologies. Guidance from a Rohm and Haas technical representative was also used during the ion exchange screening testing.

Three separate ion exchange tests were performed. The first test determined the feasibility of using ion exchange resins to remove cesium from extractant generated from sediment having an average level of cesium contamination. EG&G Idaho sample K-3 (a sediment having an average cesium concentration) was extracted for this test. The test was performed by adding an "overdose" of resin to 350 mL of extractant. The dose rate for this test was 70 g of resin per 1 L of extractant. The resin contact time used for this test was 20 hours. This dose rate and the contact time are extreme conditions designed to indicate maximum ion exchange potential. It would be unrealistic and unusually expensive to use these conditions in a scaled-up treatment system.

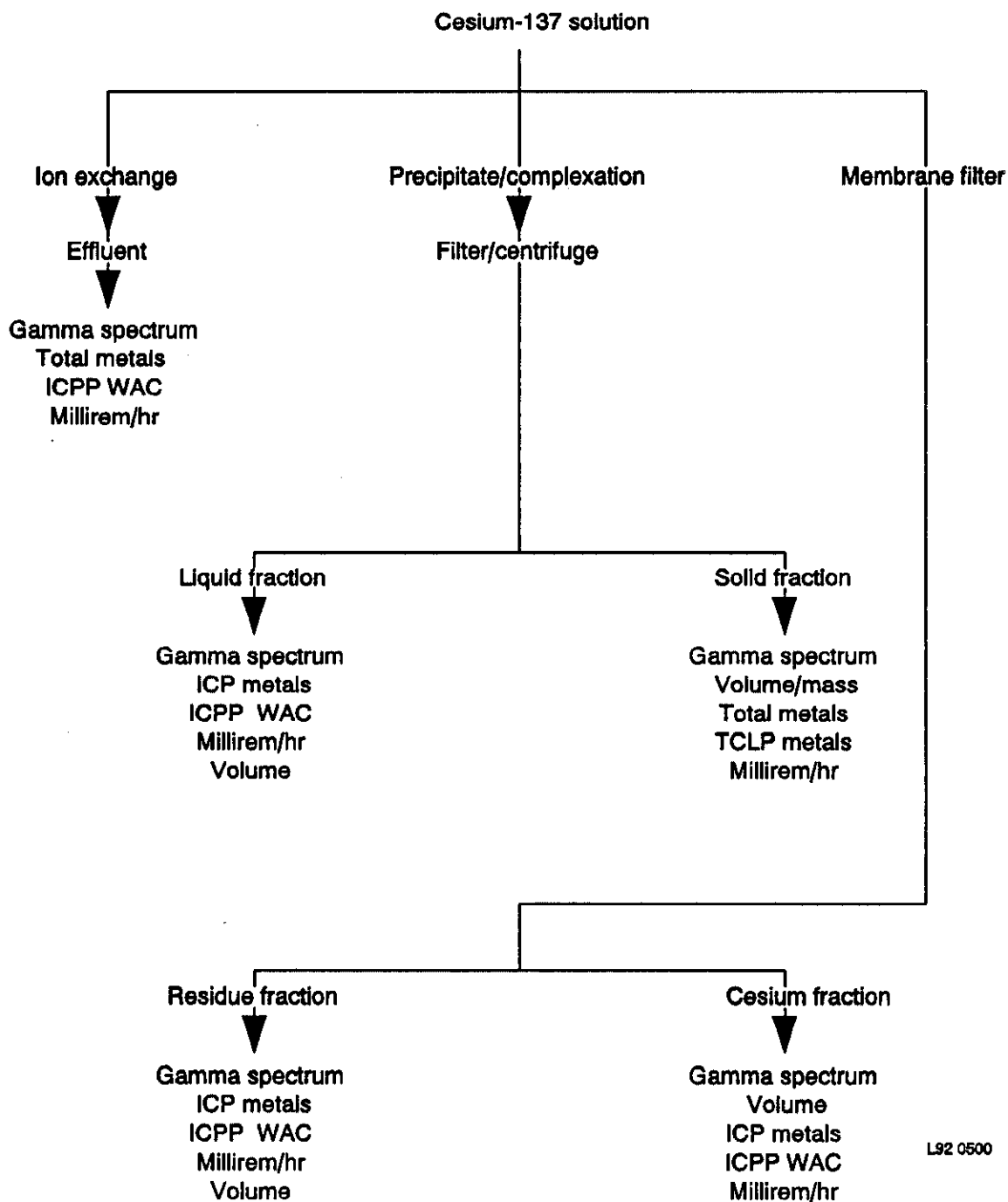
Cesium-137 concentration = average
 Duplicate samples
 Minimum sample size = 2 kg



L92 0501

Figure 2-4. Acid extraction Phase C flowsheet.

Cesium-137 removal from solution
Duplicate samples for all tests



L92 0500

Figure 2-5. Acid extraction Phase D flowsheet.

The second ion exchange test examined the relationship between dose rate and removal efficiency. The extractant used for this test was generated from material having a higher than average concentration of cesium. The resin dose rates used for this test were 1.4, 5.7, 28, and 70 g of resin per liter of extractant, and a resin contact time of 20 hours was again used. After resin-containing extractant samples were agitated for 20 hours, the resin was filtered from the extractant.

The third ion exchange test examined the relationship between contact time and cesium removal. The dose rate used for this test was 70 g/L and the extractant was generated from sediment with a higher than average cesium concentration. The contact times tested were 15 minutes, 30 minutes, and 2 hours. These times are much shorter than the 20 hour test duration used in the initial ion exchange test for good reason. As recommended by Rohm and Haas, the 20 hour duration was set to be sure that this was sufficient time for maximum ion exchange. For the contact time tests, the durations were set to be much shorter to determine if the ion exchange effectiveness for each resin increases over a duration range more typical of normal operation.

The precipitation/complexation tests were performed using ammonia phosphomolybdate for isomorphous coprecipitation. The membrane filtration (reverse osmosis) tests were performed using two different types of membrane filters. These tests were performed following procedures outlined in Section 3.4 of Appendix A.

There were some deviations in the Phase D activities from the work plan. Complexation/precipitation using the new silico-titanate material developed at Sandia National Laboratory was not possible due to the nonavailability of the silico-titanate material. This material is still under development and evaluation at Sandia. Since the silico-titanate complexation/precipitation portion of testing was dropped, tests using an additional ion exchange media (totalling 3 instead of 2 different medias) were added to the Phase D testing. These changes were performed with the approval of EG&G Idaho, DOE, and the agencies.

2.2.2 Selective Extraction Tests and Analyses

The Selective Extraction tests were performed on sediment samples with cesium activity levels that were representative of the average cesium levels in the pond. The design of the Selective Extraction tests is shown in Figure 2-6. Following the initial sample characterization and screening, only samples of -40 mesh particle sized fractions were sequentially extracted. The Selective Extraction tests were performed in accordance with the work plan with a few minor exceptions. These exceptions are noted in the following discussion.

During the initial characterization, sediment was wet screened using deionized water and stainless steel screens of mesh sizes #4, #10, #40, #100, #200 and #400. Water was continuously sprayed over the top screen. Samples of the water were collected and analyzed for radionuclides, chloride, sodium, potassium, cesium, cobalt and chromium to check for dissolution during the wet screening. The sediment samples from each size fraction were air dried and weighed to determine the weight fractions in each size fraction. These sediment fractions were then dried to constant weight at 105°C and reweighed to determine completely dry sediment fraction weights. Subsequent weighings during the sequential extractions were made after sample drying at room temperature only, without complete drying at 105°C. This prevented the possibility of modifying the soil matrix chemistry, such as removing waters of hydration from hydrated metal oxide films.

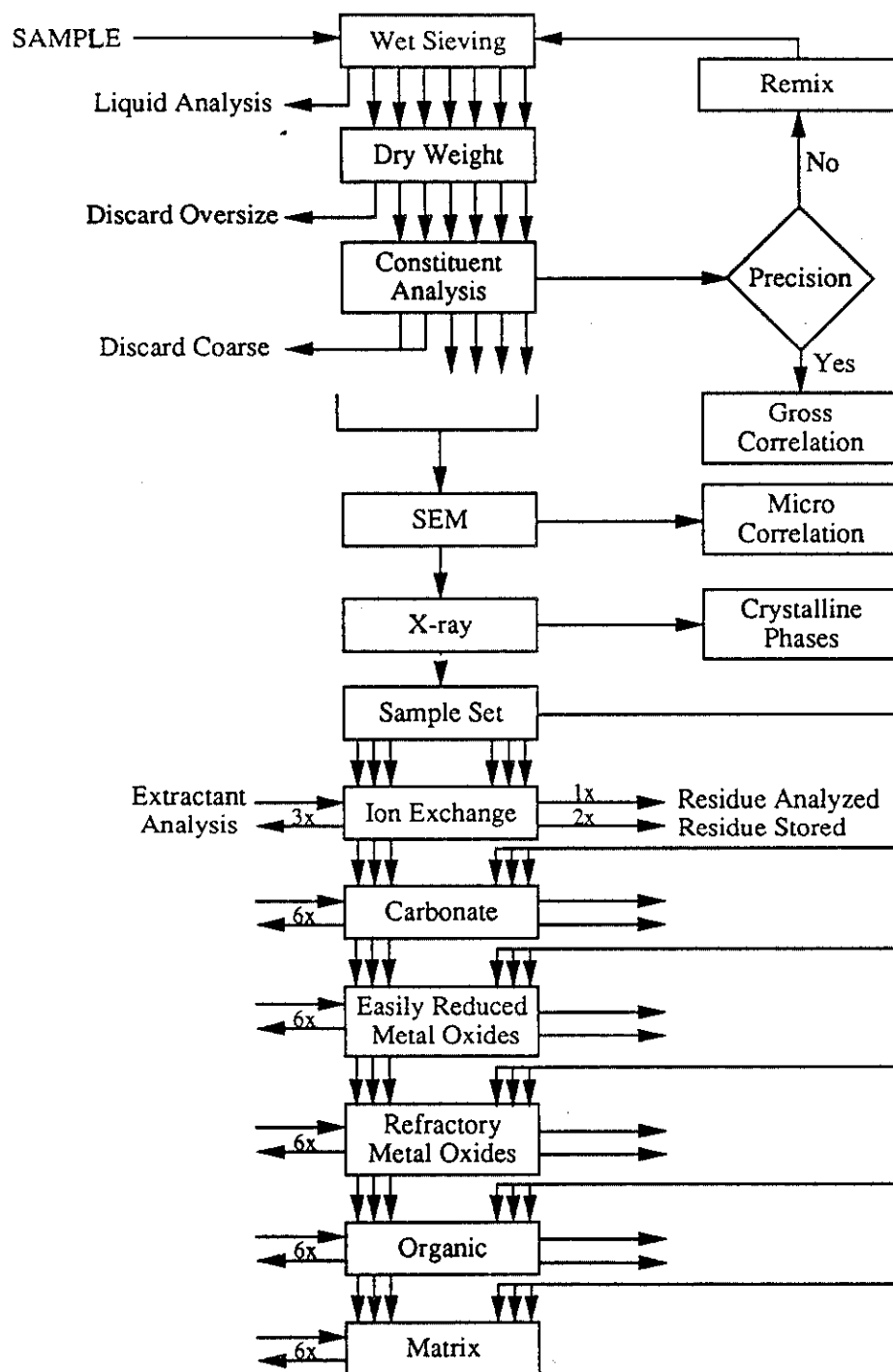


Figure 2-6. Experiment flowsheet for the selective extraction tests.

The initial characterization included determination of the particle size distribution, radionuclide and elemental distribution, scanning electron micrograph (SEM) characterization, and x-ray diffraction analysis of the major crystalline phases. Due to SEM equipment availability, the SEM characterization was performed out of sequence specified in the work plan. The SEM thus was performed as a confirmatory rather than exploratory characterization.

Approximately 1 kg (dry weight) of -40 mesh material was collected for the sequential extractions. The selection of this mesh size fraction was finalized following review and approval of EG&G Idaho, DOE, and the regulatory agencies. Only the -40 mesh material was selected for the sequential extractions for several reasons. The -40 mesh material was more homogeneous and more easily handled and analyzed using smaller sample sizes during the sequential extractions and analysis. Samples with larger particles have greater potential for variation in structure and levels of contamination. Samples with larger particles are less easily split into equivalent, representative smaller samples. In addition, it was assumed that any effective extraction scheme developed for the smaller particles would be at least as effective for larger particles.

The sequential extractions were designed to selectively attack specific mechanisms by which the sediment may be contaminated. Each extraction step was increasingly harsh, beginning with an ion exchange step that addresses the potential for the sediment to receive contamination by ion exchange. This was followed with extraction of various surface contaminants or structures from weathering, oxidation or adhesion on the particles, including the carbonate phase, the easily reducible metal oxide phase, the moderately reducible refractory oxide phase, and the organic phase. Finally the crystal lattice of the sediment particles was completely dissolved.

The sequential extractions were preceded by time-release profiles. The time-release profiles, although not specified in the test plan, were performed to establish optimal extraction times for each of the sequential extraction steps. The extraction time should be sufficiently long to allow dissolution of the desired phase as completely as reasonably possible, without causing significant undesired dissolution of other phases or readsorption of dissolved ions back onto the sediment. The extraction times specified in the work plan were adjusted in accordance with results of the time-release studies. Results of the time-release profiles are discussed in Section 5.1 and in Appendix B, Section 5.1.

Particle density determinations, also not specified in the work plan, were added in order to estimate the surface area per gram of material (specific surface area) in each particle size. This specific surface area was used to better evaluate the gross physical distribution of contamination due to surface area alone.

The samples for the sequential extractions were aliquots of the -40 mesh material of about 1 g each. All solutions were made using deionized water and analytical grade reagents. Liquid samples taken before and after the extractions were analyzed for the added reagents as well as for pH and the experimental analytes. All extractions were continuously shaken. All extractions except for the organic phase and the lattice phase extractions were conducted at room temperature. Following each extraction, the extractants were centrifuged to separate the solid and liquid material, and the solid residues were rinsed twice with 5 mL of deionized water. The rinsates were combined with the extractants. The solid residues were air dried, weighed, and stored in air-tight labeled containers. Drying was performed at room temperature rather than at 105°C, to prevent modifying the soil matrix chemistry, such as removing water of hydration from hydrated metal oxides. Sample weights on a dry basis were calculated using comparison of weight measurements following room temperature drying and drying at 105°C, done following the set screening tests.

During each sequential extraction, new samples as well as samples that experienced the prior extractions were processed. Each of the sequential extractions are summarized in the following paragraphs.

2.2.2.1 Exchangeable Phase. Six 1-g samples were extracted using 20 mL each of 1 M potassium nitrate solution at pH 7 and room temperature. Potassium nitrate was selected instead of magnesium chloride to avoid the potential for precipitation of magnesium carbonate, and instead of ammonium acetate to avoid the possible complexing of soil calcium by the acetate. Potassium ions are also the closest in size to cesium ions, which may increase the probability for effective ion exchange at sterically-controlled sites. All extractants were filtered. Three clear solution aliquots were analyzed for (a) the contaminants (cesium, cobalt, and chromium) and (b) soil matrix elements (silica, aluminum, manganese, iron, calcium, organic carbon, and inorganic carbon). The contaminants and the soil matrix elements are referred to as analytes in the following discussion. The solid residue from each extraction was handled as follows:

- One sample was analyzed for potassium and the analytes to confirm the liquid analyses
- Three samples were used in the following extractions
- Two samples were saved in air-tight containers.

2.2.2.2 Carbonate Phase. Three new 1-g samples and the three samples from the prior exchangeable phase extractions were extracted using 20 mL each of 1 M sodium acetate adjusted to pH 5 with acetic acid at room temperature. Although not specified in the work plan, this extraction was performed in potassium nitrate brine, so the potassium ions could block reabsorption of dissolved cesium back onto the sediment. The pH was adjusted as needed to pH 5 using acetic acid if the pH drifted over 0.5 pH units. The samples that were exposed to both the carbonate phase and the exchangeable phase extractions were filtered. All of these extractant solutions were analyzed, and the solid residue saved for the next step. The three new samples that experienced only the carbonate phase extraction were filtered. These extractant solutions and the solid residue from one of these samples were analyzed. The other two residue samples were saved in air-tight containers.

2.2.2.3 Easily Reducible Phase. Three new 1-g samples and the three samples from the prior extractions were extracted using 20 mL each of 0.1 M hydroxylamine hydrochloride acidified to pH 2 with 0.01 M nitric acid, at room temperature for 3 hours. Although not specified in the work plan, the extraction was performed in potassium nitrate brine, so the potassium ions could block reabsorption of dissolved cesium back onto the sediment. The pH was checked each hour and adjusted to pH 2 using nitric acid if the pH drifted over 0.5 pH units. The three samples exposed to the prior extractions were filtered, all leachates were analyzed for the analytes, and the residue was saved for the next step. The three new samples were filtered, the leachates and one residue sample analyzed for the analytes, and the other two residue samples saved in air-tight containers.

2.2.2.4 Moderately Reducible Phase. Three new 1-g samples and the three samples from the prior extractions were extracted using 20 mL each of 0.2 M ammonium oxalate acidified to pH 3 with 0.2 M oxalic acid at room temperature, and shaken for 6 hours. Although not specified in the work plan, this extraction was performed in potassium nitrate brine, so the potassium ions could block reabsorption of dissolved cesium back onto the sediment. The pH was checked each hour and adjusted to pH 3 using oxalic acid if the drift was over 0.5 pH units. The three samples exposed in the prior extractions were filtered, all leachates were analyzed for the analytes, and the residue was

saved for the next step. The three new samples were filtered, the leachates and one residue sample were analyzed for the analytes, and the other two residue samples were saved in air-tight containers.

2.2.2.5 Organic Phase. Three new 1-g samples and the three samples from the prior extractions were extracted using 15 mL each of 30% hydrogen peroxide acidified to pH 2 with 0.01 M nitric acid at 85°C. These samples were shaken for 4 hours. The pH was checked each hour and adjusted to pH 2 using nitric acid if the pH drifted over 0.5 pH units. The three samples exposed in the prior extractions were filtered, all leachates were analyzed for the analytes, and the residue was saved for the next step. The three new samples were filtered, the leachates and one residue sample were analyzed for the analytes, and the other two residue samples were saved in air-tight containers. The addition of ammonium nitrate brine during the cooling step, as specified in the work plan, was not done. Instead, the organic digestion step was done in the presence of potassium nitrate brine to block reabsorption of dissolved cesium back onto the sediment. Also, the peroxide digestion of organic material from finely divided particulate proved highly exothermic and effervescent that led to complications in handling and the loss of two samples. Adding small amounts of solid to the extractant was found to be much more reliable than adding extractant to the solid, even in diluted or minute amounts.

2.2.2.6 Lattice Phase. Three new 1-g samples and the three samples from the prior extractions were completely digested using a 1:1 mixture of concentrated nitric and hydrofluoric acid at 85°C. This was a variation from the work plan, which specified using a 3:1 mixture of concentrated hydrochloric and nitric acid (aqua regia) at 50°C until no solids were visible. The change was done to avoid unnecessary corrosion in the analytical equipment. The pH was not measured. These samples were completely digested in order to determine the levels of cesium, chromium, and cobalt in the sediment particles that remained after the selective extraction steps. These determinations were used for more accurate mass balances.

2.3 Quality Assurance/Quality Control

QA/QC activities were performed during the laboratory treatability studies according to the QA/QC programs outlined in Part A (TCT) and Part B (WINCO) in the work plan. Test and analytical procedures and QA/QC activities were conducted based on the specified Standard Operating Procedures (SOPs) and analytical methodologies. The data from the QA/QC activities is available but is not completely summarized in this report. Data validation was performed according to Validation Level C. The data quality was sufficient to reliably use the results of these studies to support the major conclusions discussed in Section 6. Results of duplicate tests and sample analyses for the Acid Extraction study are shown in the attachments of Appendix A. Results of the triplicate tests and sample analyses for the Selective Extraction study are shown in Appendix B.

3. SEDIMENT SAMPLE CHARACTERIZATION

The Acid Extraction and the Selective Extraction studies both included initial sample characterization. At TCT, sample characterization was performed in Phase A to determine the (a) particle size distribution and (b) radiological and metals (total and TCLP) levels and distribution by particle size. At WINCO, the sample characterization included (a) particle size distribution, (b) radiological and elemental distribution by particle size, (c) SEM characterization (d) characterization of major crystalline phases (by x-ray diffraction).

3.1 Particle Size Distribution

The particle size distributions were performed at TCT by dry screening. At WINCO, the particle size distributions were done by wet screening. The Standard U.S. Mesh sizes used at TCT and WINCO were as follows in Table 3-1:

Table 3-1. Standard U.S. mesh sizes.

Mesh size	Opening size (Leonard 1979)	TCT	WINCO
4	4.75 mm	x	x
8	2.36 mm	x	—
10	2.00 mm	—	x
16	1.18 mm	x	—
40	425 μ m	—	x
50	300 μ m	x	—
100	150 μ m	x	x
200	75 μ m	x	x
400	38 μ m		x

Results of the TCT particle size distribution measurements are presented in Section 4.1.1 of Appendix A. For four different samples, the particle sizes ranged from 61.5 to 73.0 Wt.% greater than 8 mesh. The arithmetic average of the distribution for the four samples was 68.5% greater than 8 mesh, which was within 1 relative % of the distribution for the composite sample (69.2% greater than 8 mesh).

Results of the WINCO particle size distribution measurements are presented in Section 4.1 of Appendix B. The particle size averaged about 71 Wt.% greater than 10 mesh. The average TCT and WINCO particle size measurements are shown in Figure 3-1. Interpolation between the mesh sizes for the WINCO results in a comparable size distribution of about 68% greater than 8 mesh for the composite WINCO sample. This is in close agreement with the TCT value of 68.5% greater than 8 mesh. There is more relative difference between the TCT and WINCO particle size measurements for the particle size ranges. This may be due in part to variations in the different samples; however, the increased relative difference is more likely due to differences in the sieving procedures. Wet sieving was performed at WINCO, compared to dry sieving performed at TCT. Wet sieving tends to more effectively remove smaller particles that, due to static charges or other forces, adhere to larger particles. These smaller particles are more effectively removed from the larger sized mesh fractions, and are formed in the smaller sized fractions.

These results confirm the results of other studies (Beller and Bessent 1991 and NRT 1992), which indicated a particle size distribution of at least 60 Wt.% of the sediment greater than 8 mesh.

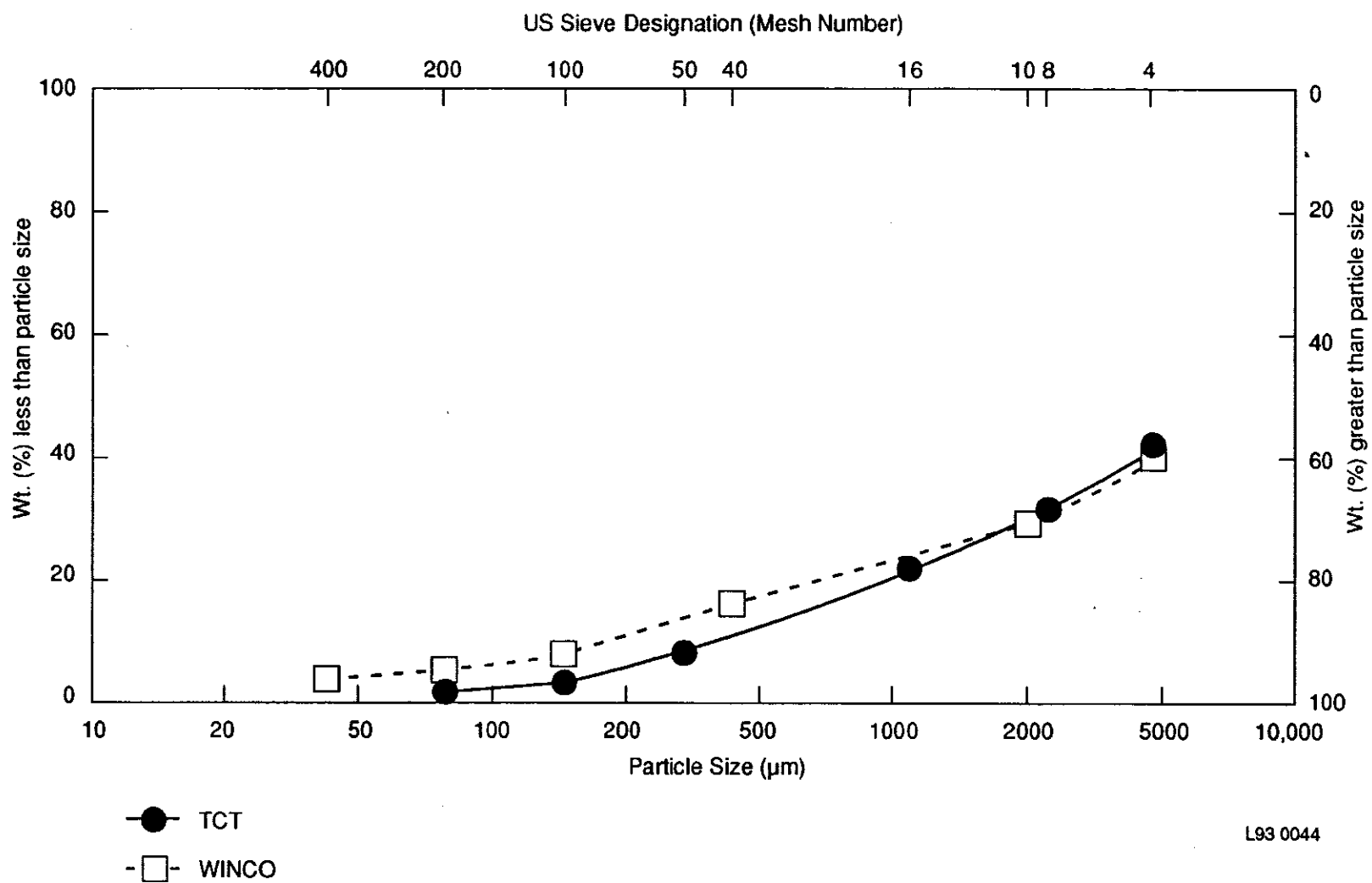


Figure 3-1. Particle size distribution from TCT and WINCO.

3.2 Radionuclide Content and Distribution

Cesium and cobalt activity distribution tests were performed by both TCT and WINCO and reported in Section 4.1.1 of Appendix A and Section 4.2 in Appendix B.

The activity distribution from TCT is shown in Table 3-2. The activity distribution from WINCO is shown in Table 3-3.

Table 3-2. Activity distribution measurements and calculations from TCT.

Sediment mesh size	Weight fraction (%) ^a	Average cesium activity (pCi/g)	Average cesium activity distribution (%)	Average cobalt activity (pCi/g)	Average cobalt activity distribution (%)
+4	57.94	3,825	22.60	228	6.15
4-8	11.21	5,965	6.85	902	4.71
8-16	8.41	10,473	8.98	3,717	14.56
16-50	14.45	18,000	26.52	5,140	34.59
50-100	4.89	38,150	18.925	9,575	21.81
100-200	1.56	45,800	7.30	11,800	8.57
<200	1.54	55,750	8.80	13,400	9.61
+8 (combined +4 and 4-8 mesh fractions)	69.15 ^b	4,172 ^c	29.45 ^d	337 ^c	10.86 ^d
-8 (combined 8-16, 16-50, 50-100, 100-200, and <200 mesh fractions)	30.85 ^b	22,432 ^c	70.55 ^d	6,204 ^c	89.14 ^d
Total sediment (all fractions combined)	100 ^b	9,805 ^c	100.00 ^d	2,147 ^c	100.00 ^d

a. Weight fraction value are from the composite sample measurements; activity measurements are from the individual sample measurements.

b. Sum of Wt.% value for the included mesh fractions.

c. Activity calculated from activities of individual mesh fractions and the corresponding Wt.% values.

d. Sum of activity distribution values for the included mesh fractions.

Note: Average cesium concentration for an analyzed composite sediment sample was 16,350 pCi/g.

Table 3-3. Activity distribution measurements and calculations from WINCO.

Sediment mesh size	Weight fraction (%) ^a	Average cesium activity (pCi/g)	Average cesium activity distribution (%)	Average cobalt activity (pCi/g)	Average cobalt activity distribution (%)
+4	59	2,400	15.0	72	2.3
4-10	12	4,100	5.2	380	2.5
10-40	14	9,700	14.4	2,400	18.4
40-100	7.4	19,000	14.9	5,000	20.3
100-200	2.0	49,000	10.4	12,000	13.1
200-400	1.6	61,000	10.3	13,000	11.4
<400	3.9	72,000	29.8	15,000	32.0
+10 (combined +4 and 4-10 mesh fractions)	71 ^b	2,700 ^c	20.2 ^d	124 ^c	4.8 ^d
-10 (combined 10-40, 40-100, 100-200, 200-400, and <400 mesh fractions)	29 ^b	26,000 ^c	79.8 ^d	6,000 ^c	95.2 ^d
Total sediment (all fractions combined)	100 ^b	9,400 ^c	100 ^d	1,800 ^c	100 ^d

a. Weight fraction values are from the composite sample measurements; activity measurements are from the individual sample measurements.

b. Sum of Wt.% value for the included mesh fractions.

c. Activity calculated from activities of individual mesh fractions and the corresponding Wt.% values.

d. Sum of activity distribution values for the included mesh fractions.

Note: Average cesium concentration for an analyzed composite sediment sample was 16,350 pCi/g.

Comparison of the activity measurements from TCT and WINCO show that there was some variation, especially in the cesium and cobalt activities calculated for the +8 and +10 mesh fractions. However, the activities calculated for the -8 (-10) mesh fractions and for the total sediment are in fairly close agreement. The greater differences in the +8 (+10) results are due to higher variations from sample to sample because of the larger sizes and smaller numbers of particles in the samples.

3.3 Elemental Content and Distribution

Elemental distribution tests were performed by both TCT and WINCO and reported in Section 4.1.1 of Appendix A and Section 4.3 in Appendix B. The chromium and total metals distribution from TCT is shown in Table 3-4. The metals distribution compared to TCLP limits from TCT is shown in Table 3-5. The elemental distribution results from WINCO are shown in Table 3-6 and Figure 3-2.

The metals content tended to increase with decreasing particle size although this was not the general trend for many of the TCLP results. Comparison of the chromium results from TCT (66 to 6,120 $\mu\text{g/g}$, or 0.066 to 0.612 Wt.%) and from WINCO (0.02 to 0.63 Wt.%) indicates relatively good agreement.

Several correlations were performed using the WINCO results to compare levels of cesium, cobalt, and chromium contamination not only to particle size but also to specific surface area and to the incidence of sediment species iron, manganese, and organic carbon. Levels of both the contaminants and the sediment species increased with decreasing particle size.

Table 3-4. Chromium and total metals distribution from TCT.

Sediment mesh size	Weight fraction (%) ^b	Chromium distribution		Total metals ^a distribution	
		Average chromium concentration ($\mu\text{g/g}$)	Concentration distribution (%)	Average total metals concentration ($\mu\text{g/g}$)	Metal concentration distribution (%)
+4	57.94	66.1	5.45	135.02	7.42
4-8	11.21	264.0	4.21	590.87	6.28
8-16	8.41	885	10.59	1,531.04	12.21
16-50	14.45	1,765	36.28	2,565.46	35.14
50-100	4.89	2,880	20.03	3,943.97	18.28
100-200	1.56	4,520	10.03	6,072.05	8.98
<200	1.54	6,120	13.41	8,009.36	11.69
Total sediment (all fractions combined)	100	703 ^c	100	1,055 ^c	100

a. Total metals includes silver, arsenic, barium, cadmium, chromium, mercury, nickel, selenium, and zinc.

b. Weight fraction values are from the composite sample measurements; concentration measurements are from the individual sample measurements.

c. Concentration calculated from concentration of the individual mesh fractions and the corresponding Wt.% values.

Table 3-5. Metals distribution in sediment fractions compared to TCLP limits from TCT.^a

Mesh size	Concentration (µg/L)											
	Silver	Arsenic	Barium	Cadmium	Chromium	Mercury	Potassium	Sodium	Nickel	Lead	Selenium	Zinc
Regulatory limits	5,000	5,000	100,000	1,000	5,000	200	—	—	—	5,000	1,000	—
+8	4.5	<310	411	6	<42	<0.10	3,272	777,000	59	<64	60	634
+16	<4	<310	626.5	16	115.5	<0.10	3,685	895,000	114.5	98	<56	1,380
+50	5	<310	635.5	32	298.5	<0.10	4,375	1,315,000	169	115	<56	1,605
+100	4	<310	765	28	303.5	<0.10	4,745	1,290,000	194.5	178.50	<56	901
+200	5.5	<310	770	34.5	328	0.185	5,340	1,340,000	243.5	123.5	<56	1,160
<200	<4	<310	866.5	38.5	323.5	1.97	6,355	1,260,000	261.5	138	<56	1,310
A-1 ^b	<4	<310	668	31	378	0.64	4,540	1,450,000	176	146	<56	1,820
A-2 ^c	10	<310	697	21	121	<0.10	3,780	1,270,000	143	104	<56	1,880
Blank	<4	<310	<200	<4	<42	<0.10	<61	<87	<40	<64	<56	<20
TCLP blank	<4	<310	<200	<4	<42	<0.10	230	850,000	<40	<64	<56	38
Sample	<4	<310	608	14	120	<0.10	3.71	847,000	111	106	<56	1,380
Duplicate	<4	<310	578	18	137	<0.10	3.68	879,000	102	<64	<56	1,320
%RPD ^d	NC ^e	NC ^e	5.1	4.0	11.0	NC ^e	0.8	3.7	9.0	NC ^e	NC ^e	4.4
Spike added	1,000	5,000	20,000	250	1,000	40	9.97	10,000	1,000	1,000	1,000	1,000
Matrix spike	1,030	5,360	19,300	261	1,130	39.1	12.68	820,000	1,200	1,050	1,090	2,400
Percent recovery	103%	107%	93%	99%	101%	98%	90%	Sample >4X Spike	109%	95%	109%	102%

a. Concentrations reported are averages of two duplicate tests.

b. Blind duplicate of +50 mesh fraction (lab #92005859).

c. Blind duplicate of +16 mesh fraction (lab #92005857).

d. RPD = relative percent difference = (measurement 1-measurement 2)/(average of measurement 1 and measurement 2) × 100%.

e. Not calculated.

Table 3-6. Elemental distribution from WINCO.

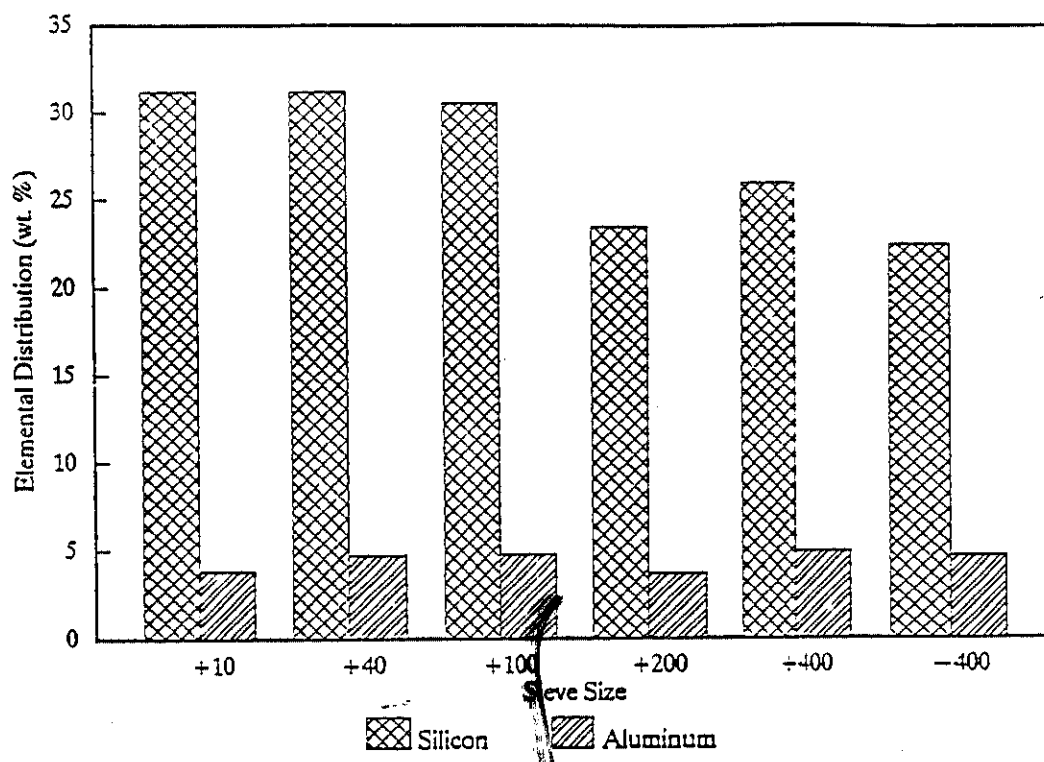
Sieve size	Elemental Wt. %							Carbon (CO ₃)	Carbon (organic)
	Aluminum	Iron	Chromium	Silicon	Manganese	Calcium			
+4	<-----No representative sample----->								
+10	3.88	1.24	0.02	31.13	0.02	2.45	0.61	0.23	
+40	4.75	1.63	0.07	31.10	0.04	1.00	0.06	0.70	
+100	4.79	1.70	0.13	30.47	0.05	1.44	0.12	1.46	
+200	3.70	2.65	0.35	23.40	0.13	3.24	0.67	3.19	
+400	4.98	2.60	0.37	25.97	0.13	3.13	0.49	3.88	
-400	4.67	3.01	0.63	22.47	0.20	2.16	0.37	4.14	

3.4 SEM Characterization

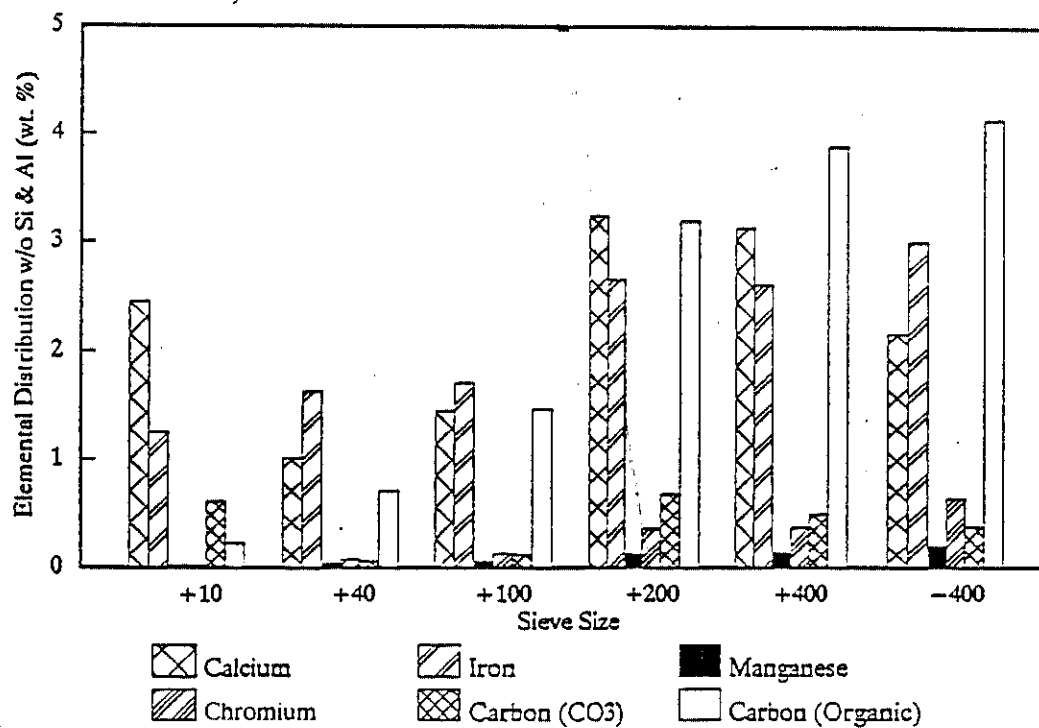
The SEM characterization was performed by WINCO and is reported in Section 4.4 of Appendix B. SEM analysis was used to provide both insight into the geometric nature of the particles and elemental maps of the as-received particle surface. By mapping the surface of the particles for matrix constituents and contaminants, correlations could be observed that are not necessarily obvious from gross assays of total elemental makeup of the soil matrix. By SEM analysis, particles from the -40 to +100 mesh fraction appear to be just minute versions of common river rock with rounded surfaces and a few pits but little or no porosity. Smaller particles from the -200 to +400 mesh fraction appeared to be mainly broken mineral fragments, not all as rounded as in the larger particle size, and some showed irregular surface deposits.

Electron dispersive spectroscopy (EDS) was then used to generate elemental spectrums. Significant presence was shown for aluminum, silicon, sulfur, potassium, calcium, barium, chromium, iron, copper, and zinc, but cesium and cobalt are not indicated. This is due to the fact that the radionuclides in these sediments occur at sub-parts-per-billion levels, and the limiting SEM sensitivity is six orders-of-magnitude greater. The radionuclides would have to be greatly concentrated at specific sites to be apparent.

Dot maps of the relative incidence of chromium for the -200 to +400 mesh samples show that there is no correlation in between chromium and iron or silicon. Silicon was ubiquitous in the sample as was expected, and the wide-spread incidence of iron suggests that an iron oxide film covers many of the particles. Dot maps were also done for a single particle in the -100 to +200 mesh size. The dot maps show a slightly elevated level of chromium above background, with coincident concentrations of iron and manganese. Calcium is barely elevated, but there is a high incidence of silicon.



a. Silicon and aluminum.



b. Other species.

Figure 3-2. Elemental distribution from WINCO.

The dot maps do not yield definitive proof of correlation of chromium with any one specific phase, but do indicate concentration of chromium in the surface deposits. Higher incidence of chromium is apparent only with weathering products that are dissolved in the sequential extractions.

The elemental mapping sequence for -200 to +400 mesh samples showed a positive correlation of chromium with the incidence of iron. Calcium and manganese are also coincident but to a lesser extent. Silicon and carbon show no positive correlation.

3.5 Major Crystalline Phases

Analysis by x-ray diffraction performed by WINCO (Section 4.5 of Appendix B) gives an indication of the probable major crystalline phases in the sample. This analysis is used for confirmation or denial of the existence of a suspect phase and the trends indicated by the analyses. The relative incidence of five functionally grouped species most commonly found in the sample is summarized by particle size in Table 3-7. Silica (α -quartz) is the dominant crystalline phase in all but the finest sieve fraction, decreasing in magnitude with particle size. Of notable exception is the -200+400 fraction that is as high in silica as the -4+10 fraction. Feldspar grains (aluminosilicates substituted with mono- and di-valent cations) and mineral weathering products such as oxides of manganese and iron, and carbonates are present in all size fractions, with a greater prevalence in the smaller size fractions. Organic carbon cannot be detected by x-ray diffraction.

The diffraction data had no apparent correlation with the incidence of contaminants, either when tested as individual crystalline species, or when grouped functionally. The data does, however, confirm the presence of all crystalline species to be targeted by the sequential extractions, and provides some insight into the relative magnitudes of each phase.

Table 3-7. Functionally grouped crystalline phases distribution by particle size.

Sieve size	Wt. %				
	SiO ₂	(Ca,NaK)CO ₃	(Fe,Mn) _x O _y	(Na,K)AlSi ₃ O ₈	CaAl ₂ Si ₂ O ₈
+4	<----- No representative sample ----->				
+10	41.7	11.1	3	6.5	3.0
+40	50.5	3.6	1.2	11.6	16.2
+100	34.3	4.5	9.7	13.9	13.1
+200	28.1	4.5	4.6	7.8	11.0
+400	42.7	2.9	3.9	21.9	9.1
-400	14.8	25.7	7.2	2.3	19.8

4. RESULTS OF ACID EXTRACTION TESTS

The results of the Acid Extraction tests performed at TCT are summarized in this section, in Section 3, and are shown in more detail in Appendix A. The Acid Extraction tests were performed in four phases denoted Phases A-D. The sediment samples were characterized in Phase A. These characterization results are summarized in Section 3 and are not included in this section. The results of Phases B-D and the preliminary Acid Extraction conceptual design and cost estimates are summarized in this section.

4.1 Phase B, Parametric and Staged Nitric Acid Extraction

Phase B tests included parametric nitric Acid Extractions and a second stage extraction, under optimum extraction conditions of solid residues from the selected optimum condition of the parametric tests. During the parametric tests, 54 nitric Acid Extractions (including duplicate tests) were performed to assess the impact of variable extraction times, extraction temperatures, and acid concentrations on the removal of cesium and cobalt concentrations from WWP sediment material. The second part of Phase B activities evaluated the effectiveness of a second stage nitric Acid Extraction to remove additional cesium and cobalt concentration from WWP sediment material.

Only samples of -8 mesh sediment were extracted. These samples were generated during Phase A. The -8 mesh particle size fraction was selected to match the desired physical separation goal of the ROD, which was to physically separate at least 60% of the material and chemically treat the remaining 40% or less. From the Phase A size distribution tests, it was confirmed that at least 60 Wt.% of the sediment was greater than 8 mesh and could be physically separated from the -8 mesh material that had much higher contamination levels.

The cesium and cobalt extraction efficiency of the different parametric conditions is shown in Figures 4-1 and 4-2. Removal efficiencies were calculated using estimated radionuclide concentrations for -8 mesh WWP sediment material from Phase A radionuclide data and the measured cesium and cobalt activities following the extractions. The highest average cesium removal efficiency was 80.5%, achieved by the 8-hour extraction tests performed at approximately 95°C. Removal efficiencies associated with the 8-hour, 95°C tests seemed to be somewhat independent of acid strength. Increasing the acid strength from 3 M to 12 M did not significantly improve radionuclide removal efficiencies significantly.

A qualitative consideration of full scale materials of construction and operations was done to evaluate which of the time, temperature, and concentration parameters are most significant relative to full-scale system design, cost, operation, and safety. The extraction time, within the tested ranges, was least significant. The concentration was considered slightly more significant than the temperature. Based upon the removal effectiveness observations and the design, cost, operation, and safety considerations, the optimal nitric acid conditions were defined as (a) acid concentration, 3 M, (b) extraction duration, 8 hours and (c) extraction temperature, 95°C. This selection was approved by DOE, EPA, and IDHW prior to implementation.

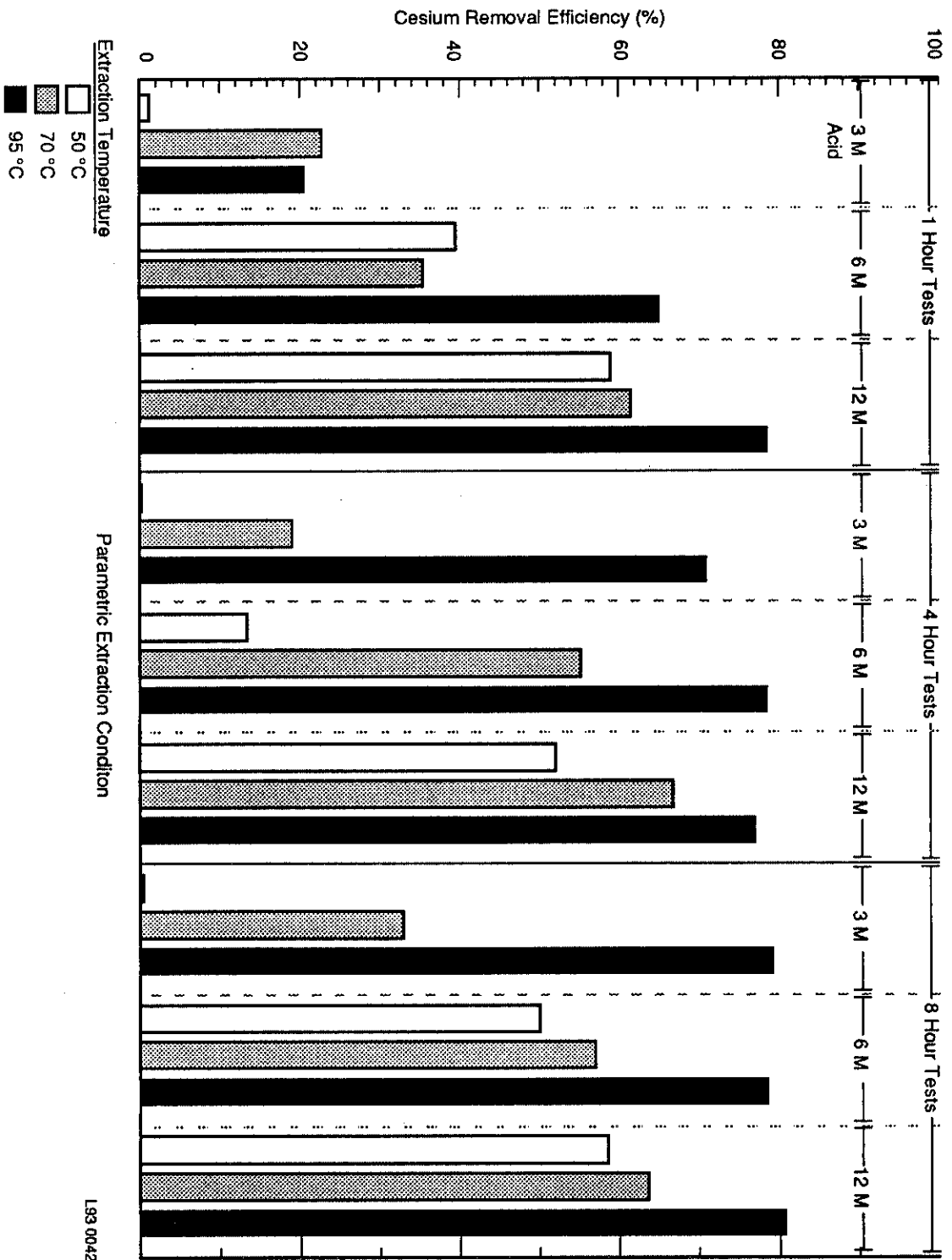


Figure 4-1. Cesium removal efficiencies for 1, 4, and 8-hour extraction tests.

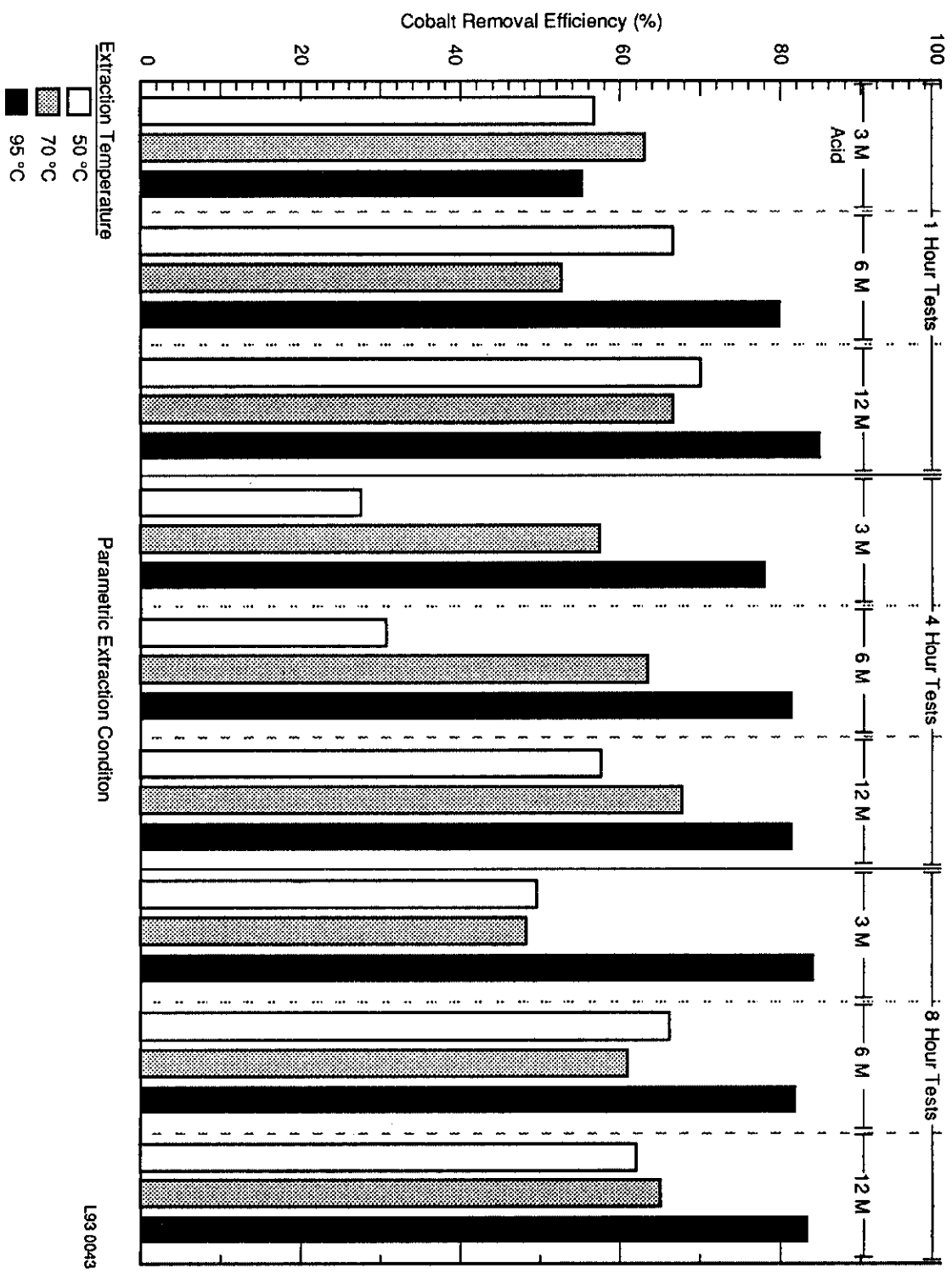


Figure 4-2. Cobalt removal efficiencies for the 4-hour extraction tests.

The total metals, TCLP metals, ICPP, and % solids dissolved results associated with the optimal extraction conditions (3 M nitric acid, 8 hour extraction time, and 95°C) are presented in Section 4.2 of Appendix A. The TCLP metals results for the treated sediment are shown in Table 4-1. As shown in Table 4-2, the resulting extractant from the 8 hour-3 M-95°C extraction, untreated, will not readily meet the ICPP WAC. Parameters that exceed ICPP WAC include arsenic, cadmium, chromium, and lead. Of these, chromium exceeds the ICPP WAC by a factor of over a 100. Chloride levels may also exceed ICPP WAC although this cannot be determined from the analytical result due to a high detection limit. Results for uranium and total plutonium are not yet available from the laboratory.

The amount of the sediment matrix that was dissolved under the optimal conditions averaged 22 Wt.%, significantly higher than the sediment dissolution results of around 8.5% from the earlier bench-scale tests.

The results of the second stage extraction testing are tabulated in Section 4.2 of Appendix A. The total cesium removal increased to 88.9-91.1% for the duplicate samples, averaging 89.9%. The total cobalt removal was 90.7-93.5% for the duplicate samples, averaging 92.1%. The addition of a second extraction to the proposed treatment train is beneficial by increasing the total contaminant removal although (a) dissolution of the sediment matrix dissolution during this second extraction was 13%, and (b) the extractant from this second extraction, like that from the first extraction, did not meet the ICPP WAC. The combined sediment matrix dissolution from both extractions totalled 32% of the initial sediment.

4.2 Phase C, Optimal Nitric Acid Extraction and Precipitation and ICPP Acceptability

Phase C activities can be divided into three tests for ease of data presentation. The first Phase C test involved the extraction of larger (2 kg) samples of WWP sediment material possessing average and maximum radioactive contamination. The second Phase C tests (Phase C-2) evaluated the ability of pH adjustment by NaOH addition to precipitate dissolved materials and remove cesium and cobalt from generated extractant liquids. The last Phase C tests reinvestigated cesium and cobalt distribution and how it changed in WWP sediment material after nitric Acid Extraction under optimal conditions.

Results of these tests are reported in Section 4.3 of Appendix A. Cesium removal efficiency for the average-activity sediment (Sample K-3) was slightly higher at 81.0-87.1% (averaging 84.1%) than the results of the Phase B tests, done with smaller samples. The amount of sediment matrix that dissolved was similar, at 20%, to sediment dissolution in Phase B.

For the high-activity samples the cesium removal efficiency was 45.1-58.3% (averaging 51.7%), and the cobalt removal efficiency was 63.8-64.8% (averaging 64.3%). The conclusion that can be drawn from this data is that as cesium concentration increases, the performance of the optimal extraction parameters are less effective. An increase in cesium concentration by a factor of 4.6 results in a 20% decrease in the overall removal efficiency. The sediment dissolution for the high-activity sediment was significantly higher, at 29-38% (averaging 33.5%), than for the average-activity sediment. This may be related in part to foaming and offgassing observed during the high-activity sediment extractions that was not observed during the average-activity extractions.

Table 4-1. TCLP metals results for Phase B, 8 hr-3 M-95°C.

Parameter	TCLP limits	Concentration (mg/L)	
		8 hr-3 M-95°C	8 hr-3 M-95°C (Dup)
Arsenic	<5.0	<0.071	<0.071
Barium	<100.0	21.6	28.8
Cadmium	<1.0	0.024	0.025
Chromium	<5.0	13.2	13.5
Lead	<5.0	0.147	0.165
Mercury	<0.2	0.0541	0.0542
Selenium	<1.0	0.103	0.059
Silver	<5.0	0.278	0.322

The TCLP metals results for the extracted solid residues from the average-cesium and high-cesium samples are shown in Table 4-3. The extracted solid residue from the average-cesium sediment is not TCLP toxic, but the extracted solid residue from the high-cesium sediment exceeded the TCLP limits for two methods. The chromium level exceeded the TCLP limit by a factor of 80% for one of the analyses. The TCLP limit for mercury was exceeded by as much as 2 to 3 times.

The ICPP WAC results for the average cesium (C1) and high cesium (C2) extractants are shown in Table 4-4. For the average cesium extractant, the barium, cadmium, chloride, and sulfate levels from at least one of the duplicate samples exceeded the ICPP WAC. For the high cesium extractant, the barium, cadmium, lead, mercury, and sulfate levels exceed the ICPP WAC. For all samples, the pH is below the minimum acceptable level of 2. Even after adjustment of the extractants pH to 9, the extractants still fail to meet the ICPP WAC. This pH adjustment, however, resulted in 54.4% cesium removal and 79.3-99.6% cobalt removal from the extractant due to precipitation of significant amounts of hydroxide sludge.

The sieving of the solid residue from the C1 tests shows an interesting phenomenon. Where as analysis of untreated, sieved fractions showed that only about 10% of the total cesium and cobalt was in the minus 200 fraction, after extracting the material one time, approximately 47% of the remaining total cesium and cobalt was in the minus 200 fraction. The cobalt and cesium, in part, seems to have been transferred to the smallest sieve size, or at least, was least more effectively removed from the larger particles. This possibly is the result of cobalt and cesium-containing fines being washed off of the larger particle sizes, thereby freeing it and allowing its migration to the smallest sieve fraction.

Table 4-2. ICPP acceptance criteria results for Phase B, 8 hr-3 M-95°C extractant.

Parameter	Acceptance criteria limits ^a	Concentration (mg/L unless otherwise specified)	
		8 hr-3 M-95°C extractant	8 hr-3 M-95°C extractant (Dup)
Arsenic	<5.0	8.42	7.19
Barium	<100.0	60.5	76.0
Cadmium	<1.0	1.28	1.72
Chromium	<5.0	575	755
Lead	<5.0	16.9	18.7
Mercury	<0.2	0.019	0.031
Selenium	<1.0	0.780	<0.560
Silver	<5.0	0.64	3.54
Chloride	<50.0	<500	<500
Fluoride	<200.0	6.8	10.3
Sulfate	<100.0	<100	<100
Sodium + Potassium	1 M (any combination of the two)	Na = 0.0014 g/L (0.000061 M) K = .38 g/L (0.0097 M)	Na = 0.0012 g/L (0.000052 M) K = .357 g/L (0.0091 M)
Uranium-235	<5 E-3 g/L	9.05 E-5 g/L	3.62 E-5 g/L
Total plutonium	<5 E-3 g/L	7.86 E-3 g/L	8.84 E-3 g/L
Iodine-131	Below detection limit	<0.849 pCi/mL	<0.877 pCi/mL
Gross beta ^b	<1 E+7 beta/min/mL	3.02 E-3 ± 2.60 E-5 µCi/mL (6,700 ± 58 beta/min/mL)	3.09 E-3 ± 2.60 E-5 µCi/mL (6,850 ± 58 beta/min/mL)
pH	<4 but >2, units	<2	<2
Dissolved organic carbon	No limit presently	870 mg/L	1,180 mg/L
Phosphate	<950 mg/L	1.0 mg/L	0.37 mg/L

a. Acceptance criteria limits specified for offsite shipping from other INEL facilities by Westinghouse Idaho Nuclear Company, Inc.

b. Backup data for gross beta results are presented in Attachment K.

Table 4-3. TCLP metals results for Phase C extraction tests.

Parameter	TCLP limits	Concentration (mg/L)				
		Test identification				
		C1	C1 Dup	C2	C2 Dup	C2 Blind Dup
Arsenic	<5.0	<0.071	<0.071	<0.071	<0.071	<0.071
Barium	<100.0	0.936	0.942	0.857	0.850	0.925
Cadmium	<1.0	0.018	0.008	0.257	0.271	0.313
Chromium	<5.0	1.29	1.05	8.93	3.60	10.60
Lead	<5.0	0.144	0.079	0.588	0.550	0.717
Mercury	<0.2	0.023	0.023	0.428	0.567	0.558
Selenium	<1.0	<0.001	<0.001	<0.001	<0.001	<0.001
Silver	<5.0	0.281	0.199	0.290	0.286	0.205

Table 4-4. ICPP WAC results for Phase C extraction tests.

Parameter	Acceptance criteria limits ^a	Concentration (mg/L unless otherwise shown)			
		Test identification			
		C1 Extractant	C1 Extractant Dup	C2 Extractant	C2 Extractant Dup
Arsenic	<5.0	4.551	1.861	7.21	8.05
Barium	<100.0	124	80.5	75.5	83.0
Cadmium	<1.0	1.07	0.811	4.48	4.44
Chromium	<5.0	1,390	2,864	3,660	3,550
Lead	<5.0	39.0	26.4	120.0	117.0
Mercury	<0.2	5.44	4.42	31.4	28.3
Selenium	<1.0	0.059	0.051	0.160	0.096
Silver	<5.0	0.240	0.08	0.88	0.56
Chloride	<50.0	<1000	<1000	16.4	<50
Fluoride	<200.0	<2	2.39	<2	<2
Sulfate	<100.0	<500	<100	2,370	1,730
Sodium + Potassium	1 M (any combination of the two)	Na = 0.108 g/L (0.0047 M) K = 0.286 g/L (0.0073 M)	Na = 0.062 g/L (0.0027 M) K = 0.544 g/L (0.014 M)	Na = 0.084 g/L (0.0031 M) K = 0.408 g/L (0.0105 M)	Na = 0.089 g/L (0.0039 M) K = 0.396 g/L (0.0102 M)
Uranium-235	<5 E-3 g/L	72.1 pCi/L (3.33 E-5 g/L)	158 pCi/L (7.29 E-5 g/L)	45.0 pCi/L (2.07 E-5 g/L)	432 pCi/L (19.9 E-5 g/L)
Total plutonium	<5 E-3 g/L	0.0178 g/L	0.00868 g/L	0.0138 g/L	0.0596 g/L
Iodine-131	Below detection limit	<2.63 pCi/mL	<0.765 pCi/mL	<16.7 pCi/mL	<30.3 pCi/mL
Gross beta ^b	<1 E+7 beta/min/mL	4.83 E-3 ± 3.36 E-5 µCi/mL (10,700 ± 75 beta/min/mL)	4.98 E-3 ± 3.39 E-5 µCi/mL (11,100 ± 76 beta/min/mL)	2.20 E-2 ± 7.50 E-5 µCi/mL (48,800 ± 167 beta/min/mL)	2.12 E-2 ± 7.79 E-5 µCi/mL (47,100 ± 173 beta/min/mL)
pH	<4 but >2, units	<2	<2	<2	<2
Dissolved organic carbon	No limit presently	2,250 mg/L	1,590 mg/L	9,440 mg/L	11,230 mg/L
Phosphate	<950 mg/L	<1,000 mg/L	<1,000 mg/L	<1,000 mg/L	<1,000 mg/L

a. Acceptance criteria limits specified for off-site shipping from other INEL facilities by Westinghouse Idaho Nuclear Company, Inc.

b. Backup data for gross beta results presented in Attachment K.

4.3 Phase D, Treatment of Extractant Solution and ICPP Acceptability

Phase D is described in terms of three different tasks. The first task (Phase D-1) addresses the capability of ion exchange resins to remove cesium and cobalt concentrations from generated extractants. The second task (Phase D-2) involved the evaluation of two precipitation agents, and sodium phosphomolybdate, to remove cesium and cobalt from generated extractants. The last task (Phase D-3) was performed to evaluate the ability of reverse osmosis membranes to concentrate cesium and cobalt from nitric acid extractants.

Three ion exchange resins, which in other applications have been proven to remove cesium from solutions, were tested: IR-120 Plus, C-3, and cesium-100. Ion exchange resins will react explosively with strongly oxidizing materials such as nitric acid. Because of this, the pH of the extractants had to be adjusted. The resin manufacturer recommended that the cesium-100 resin not be exposed to a pH of less than 9 and that the IR-120 and C-3 resins not be exposed to a pH of less than 1. TCT adjusted the extractant samples used for the ion exchange tests to these values. When TCT adjusted the extractant pH to 1, a slight amount of a very fine precipitate was formed. TCT did not separate this precipitate from the extractant before the resin tests and the filter used by TCT to separate the resin from the extractant after the resin tests allowed the fine precipitate to pass through.

Only the cesium-100 showed an ability to remove cobalt and cesium from the extractant generated from the C1 tests, removing 67% of the cesium and 99% of the cobalt. When the C-3 and cesium-100 resins were again tested, this time using extractant generated from the C2 tests, both resins showed an ability to reduce cobalt and cesium concentrations. The removal efficiency of the cesium-100 resin was much greater than that for the C3 resin. Contact time between resin and extractant also significantly affected the removal efficiency. The 2-hour contact time achieved a removal efficiency approximately 25% greater than the 15-minute contact time.

Treated extractants from all of the ion exchange tests failed to meet all of the ICPP WAC, as shown in Table 4-5. Parameters that are exceeded for on or more of these treated extractants include levels of cadmium, chromium, lead, mercury, chloride, sulphate, sodium, and pH.

Ammonium phosphomolybdate complexation of the average cesium extractant followed by pH adjustment (to pH 9.0 with NaOH) of the extractant produced excellent results for cesium and cobalt removal. Ninety-six percent of the cesium and 99% of the cobalt was removed from the extractant. An overall removal efficiency of 97% was achieved. However, the extractant following complexation did not meet all ICPP WAC, as shown in Table 4-6. Acceptance criteria that were not met include limits for arsenic, sulfate, and pH levels.

For the reverse osmosis tests, two reverse osmosis (RO) membranes, designated BQ001 and MX07, were tested and their ability to remove cesium and cobalt from the extractant was determined. Typically, RO membranes separate two circulating fluids, one having a high concentration of a solute (cesium and cobalt in this case), the other a low concentration of the material. The RO membrane has a pore size small enough to block the passage of the movement of the solute but large enough to allow the passage of the solvent. Under atmospheric pressure, the normal direction of solvent movement in this system would be from high solute concentration to low solute concentration. Reverse osmosis processes succeed in reversing this solvent flow when the pressure in the low concentration side (encouraging solvent flow from high to low) is greater than the osmotic pressure (encouraging solvent flow from low to high). TCT modeled this process using a TCLP filtration apparatus pressurized to 100 psi.

Table 4-5. ICPP WAC results for Phase D ion exchange resin tests maximum concentration extractant.

Parameter	Acceptance criteria limits ^a	Concentration (mg/L unless otherwise stated)					
		Test identification					
		C3	C3 Dup	CS100	CS100 Dup	IR120	IR120 Dup
Arsenic	<5.0	2.53	1.93	0.72	0.72	2.50	1.88
Barium	<100.0	71.1	48.9	6.69	8.49	68.8	45.4
Cadmium	<1.0	1.63	1.17	0.90	0.80	1.63	1.05
Chromium	<5.0	1120	738	14.8	58.7	880	624
Lead	<5.0	14.6	7.51	<0.022	<0.022	9.97	7.23
Mercury	<0.2	2.73	1.89	0.582	0.352	2.40	0.190
Selenium	<1.0	0.232	0.197	<0.056	<0.056	.217	0.167
Silver	<5.0	0.809	0.475	<.007	0.063	0.577	0.413
Chloride	<50.0	<500	<500	<50	<50	74.7	59.2
Fluoride	<200.0	11.1	10.6	7.14	4.42	11.6	11.6
Sulfate	<100.0	1,354	1,120	678	517	665	310
Sodium + Potassium	1 M (any combination of the two)	Na = 64.0 g/L (2.7 M) K = 6.64 g/L (0.017 M)	Na = 68 g/L (3.0 M) K = 0.518 g/L ((0.013 M)	Na = 85 g/L (3.7 M) K = .617 g/L (0.016 M)	Na = 86.5 g/L (3.8 M) K = 0.572 g/L (0.015 M)	Na = 79.5 g/L (3.5 M) K = .64 g/L (0.016 M)	Na = 65 g/L (2.8 M) K = 0.54 g/L (0.014 M)
Uranium-235	<5 E-3 g/L	131 pCi/L (6.05 E-5 g/L)	85.6 pCi/L (3.95 E-5 g/L)	185 pCi/L (8.54 E-5 g/L)	36.0 pCi/L (1.66 E-5 g/L)	90.1 pCi/L (4.16 E-5 g/L)	18.0 pCi/L (8.3 E-6 g/L)
Total plutonium	<5 E-3 g/L	1.68 E-3 g/L	1.17 E-3 g/L	1.38 E-4 g/L	1.38 E-4 g/L	3.88 E-3 g/L	1.77 E-4 g/L
Iodine-131	Below detection limit	<3.75 pCi/mL	<5.27 pCi/mL	<0.735 pCi/mL	<0.843 pCi/mL	<2.76 pCi/mL	<2.82 pCi/mL

Table 4-5. (continued).

Parameter	Acceptance criteria limits ^a	Concentration (mg/L unless otherwise stated)					
		Test identification					
		C3	C3 Dup	CS100	CS100 Dup	IR120	IR120 Dup
Gross beta ^b	<1 E+7 beta/min/mL	1.39 E-3 ± 2.49 E-5 µCi/mL (3,090 ± 55 beta/min/mL)	1.69 E-3 ± 2.09 E-5 µCi/mL (3,750 ± 46 beta/min/mL)	2.45 E-4 ± 7.96 E-6 µCi/mL (544 ± 18 beta/min/mL)	2.11 E-4 ± 7.41 E-6 µCi/mL (468 ± 16 beta/min/mL)	3.09 E-3 ± 2.98 E-5 µCi/mL (6,860 ± 66 beta/min/mL)	1.86 E-3 ± 2.19 E-5 µCi/mL (4,130 ± 49 beta/min/mL)
pH	<4 but >2, units	<2	<2	9	9	<2	<2
Dissolved organic carbon	No limit presently	4,070	4,395	780	540	1,130	8,180
Phosphate	<950	365 µg/L	664 µg/L	214 µg/L	1,250 µg/L	1,020 µg/L	699 µg/L

a. Acceptance criteria limits specified for offsite shipping from other INEL facilities by Westinghouse Idaho Nuclear Company, Inc.

b. Backup for gross Beta analyses is presented in Attachment K.

Table 4-6. ICPP WAC results for Phase D complexation tests.

Parameter	Concentration (mg/L unless otherwise stated)		
	Acceptance criteria limits ^a	Test identification	
		D4*	D4 Dup*
Arsenic	<5.0	7.95	6.70
Barium	<100.0	12.3	5.32
Cadmium	<1.0	<0.05	<0.05
Chromium	<5.0	135	<0.30
Lead	<5.0	<1.1	<1.1
Mercury	<0.2	.028	.004
Selenium	<1.0	<.560	<0.560
Silver	<5.0	<0.35	<0.35
Chloride	<50.0	<50.0	<50.0
Fluoride	<200.0	4.05	9.70
Sulfate	<100.0	558	561
Sodium + Potassium	1 M (any combination of the two)	Na = 3.6 g/L (0.16 M) K = .344 g/L (0.088 M)	Na = 1.12 g/L (0.049 M) K = 477 g/L (0.012 M)
Uranium-235	<5 E-3 g/L	9.14 E-5 g/L	9.37 E-5 g/L
Total plutonium	<5 E-3 g/L	81 pCi/L (3.74 E-5 g/L)	108.1 pCi/L (4.99 E-5 g/L)
Iodine-131	Below detection limit	<0.572 pCi/mL	<0.392 pCi/mL
Gross beta ^b	<1 E+7 beta/min/mL	4.39 E-3 ± 3.47 E-6 µCi/mL (9,750 ± 8 beta/min/mL)	2.55 E-5 ± 2.62 E-6 µCi/mL (57 ± 6 beta/min/mL)
pH	<4 but >2, units	9.0	9.0
Dissolved organic carbon	No limit presently	610 mg/L	650 mg/L
Phosphate	<950 mg/L	828 µg/L	189 µg/L

* These samples were neutralized with 10 N NaOH.

a. Acceptance criteria limits specified for offsite shipping from other INEL facilities by Westinghouse Idaho Nuclear Company, Inc.

b. Backup for gross Beta analyses presented in Attachment K.

Extractants from the C2 tests were pressurized through each of the two membranes. Neither of the membranes was successful in separating out significant quantities of contaminants. The membrane MX07 was tested only one time because despite several tries, the maximum allowable pressure for the batch membrane extractor of 100 psi was not sufficient to push any fluid through the membrane. The ICPP WAC results are shown in Table 4-7. Limits that were exceeded for on or more of the samples include arsenic, barium, cadmium, chromium, lead, mercury, sulfate, and phosphate.

4.4 Preliminary Acid Extraction Conceptual Design and Costs

The preliminary conceptual design, anticipated performance, and estimated cost of a proposed WWP sediment treatment train are summarized in this section, and discussed in more detail in Section 5 of Appendix A. This preliminary design is conceived to achieve the best results indicated by the treatability tests. However, based on the results of the treatability tests, this preliminary conceptual design will not produce treated solid residues from Acid Extraction that meet the assumed ROD goal for average cesium activity of less than 690 pCi/g for the sediment backfilled to the pond. In addition, the liquid extract will not readily meet ICPP WAC criteria. This implies additional treatment and/or managed disposal of both solid and liquid residues from the Acid Extraction. A process flow diagram (PFD) has been developed using treatability data generated during pilot study activities and other engineering data. The principal unit operations associated with the WWP treatment train are as follows:

8 Mesh Screening Apparatus - This apparatus separates the +8 mesh from the -8 mesh WWP sediment material after physical separating. The fines from both of the sediment material fractions will be further processed for the removal of ROD target contaminants of concern.

3/8" Screening Apparatus - The +8 mesh material from the 8 mesh screening apparatus is fed to this unit operation for further physical separation. The +3/8" material may be fed back to the WWP without treatment assuming that the cesium concentration is <690 pCi/g (ROD cleanup concentration). This assumption was not verified during the treatability studies. The -3/8" material will be introduced to a log washer for further mechanical processing.

Log Washer - The -3/8" material from the 3/8" screening apparatus will be fed to the log washer where constant contact between sediment particles in conjunction with high pressure water will aid in the stripping of the outer layer of sediment material. It is this outer layer of sediment material that contains a significant concentration of cesium-137 in the coarse fraction sediment material. Since most of the cesium load is associated with the stripped material, it will be sent to acid units. The cleaned -3/8" material may meet the ROD goal of 690 pCi/g and be returned to the WWP. This assumption has not been verified by the treatability studies.

Acid Extractor/Washer #1 - The stripped layer of the -3/8" material from the log washer and the -8 mesh material from the screening apparatus will be combined into this steam heated reaction vessel. HNO₃ and Dilution H₂O will be pumped to this vessel and the first extraction will begin.

The conditions associated with the acid extraction process are 95°C extraction temperature, 8-hour extraction time, and 3 M HNO₃ extractant. The expected cesium removal efficiency of this process, as extrapolated from the treatability data, is approximately 84%.

Table 4-7. ICPP acceptance criteria results for Phase D membrane filter tests.

Parameter	Acceptance criteria limits ^a	Test identification		
		BQ001	BQ001 Dup	MX07
Arsenic	<5.0	4.90	3.65	3.48
Barium	<100.0	139.0	97.3	90.7
Cadmium	<1.0	2.58	1.88	2.38
Chromium	<5.0	2690	1780	1570
Lead	<5.0	30.4	21.6	19.7
Mercury	<0.2	4.46	3.14	2.82
Selenium	<1.0	0.518	0.385	0.409
Silver	<5.0	1.29	1.04	0.95
Chloride	<50.0	<500	<500	<500
Fluoride	<200.0	<2	8.51	11.6
Sulfate	<100.0	839	<100	<100
Sodium + Potassium	1 M (any combination of the two)	Na = 0.24 g/L (0.010 M) K = 0.687 g/L (0.018 M)	Na = 0.180 g/L (0.0078 M) K = 0.435 g/L (0.011 M)	Na = 0.079 g/L (0.0034 M) K = 0.433 g/L (0.011 M)
Uranium-235	<5 E-3 g/L	— ^b	— ^b	— ^b
Total plutonium	<5 E-3 g/L	— ^b	— ^b	— ^b
Iodine-131	Below detection limit	— ^b	— ^b	— ^b
Gross beta	<1 E+7 beta/min/mL	6.15 E-3 ± 3.84 E-5 µCi/mL (13,700 ± 85 beta/min/mL)	4.30 E-3 ± 3.17 E-5 µCi/mL (9,550 ± 70 beta/min/mL)	4.14 E-3 ± 3.08 E-5 µCi/mL (9,190 ± 68 beta/min/mL)
pH	<4 but >2, units	<2	<2	<2
Dissolved organic carbon	No limit presently	1,920 mg/L	1,640 mg/L	1,320 mg/L
Phosphate	<950 mg/L	1,900 µg/L	849 µg/L	2,810 µg/L

a. Acceptance criteria limits specified for offsite shipping from other INEL facilities by Westinghouse Idaho Nuclear Company, Inc.

b. Not available; sample exhausted prior to analysis of these parameters.

It is anticipated that the first stage acid extraction process would be operated to complete two batches of sediment per day. Each batch cycle would include 1-hour load operation, an 8-hour acid extraction, a 1-hour wash, and finally a 1-hour sediment unloading operation.

Extractor #1 Thickener - After the first extraction and wash takes place, the sediment will pass through this unit operation from the Acid Extractor/Washer #1. In the Extraction #1 Thickener, the extracted sediment material is separated from the extractant and subsequently transferred to the second stage acid extraction unit.

Acid Extractor/Washer #2 - In this unit the sediment is extracted a second time. The conditions and mode of operation in this unit are identical to those used with the first extraction unit. The cesium removal efficiency identified through treatability studies for the second stage extraction unit is approximately 56%.

Extractor #2 Thickener - The treated WWP sediment from the second acid extractor and washwater are passed through this unit operation. The extracted material is now pumped to a Belt Filter Press. Extractant liquid is subsequently pumped to the extractant storage tank.

Belt Filter Press - This unit dewateres the second extracted sediment. The dilute acid wash is pumped to the Nitric Acid Extractant Storage Tank. The twice-treated sediment is at this stage returned to the WWP.

Nitric Acid Extractant Storage Tank - This tank holds the HNO_3 extractant from the first and second acid extraction phases plus the dilute acid washwater from the Belt Filter Press.

From this unit operation, three extractant treatment scenarios are possible and are addressed below.

Scenario #1 - Idaho Chemical Processing Plant

From the Nitric Acid Extractant Storage Tank the extractant is delivered to the ICPP.

Scenario #2 - Ion Exchange

Floc-Clarifier - Extractant is pumped to the floc-clarifier where 50% NaOH is pumped from the NaOH feed system and the pH adjusted to 9.0. The pH of the extractant is adjusted so that the liquid is compatible with the ion exchange resin associated with this scenario. During the pH adjustment step, metal hydroxide sludge is generated. The sludge generated settles out in the floc-clarifier resulting in separation of sludge from supernatant.

Dewatering Unit (Filter Press) - The metal hydroxide sludge generated is pumped to this unit operation where the filtrate from this operation joins the extractant from the floc-clarifier. The dewatered sludge is sent to further processing evaluated during the pilot study.

Filter Units - The extractant from the pH adjustment floc-clarifier and the filtrate from the filter press are final-filtered before being sent to an Ion Exchange System. The filter units are intended to remove suspended solids from the extractant liquid that could impact the performance of the ion exchange units.

Ion Exchange - The final filtered extractant that has been pH-adjusted is sent through a selective Ion Exchange Resin. The flow stream is then monitored for analytes of choice and the treated extractant is stored in the Treated Extractant Storage Tank.

Scenario #3 - Chemical Precipitation/Complexation

Floc-Clarifier #1 - Extractant from the extraction phase is pumped from storage to the floc-clarifier where ammonium phosphomolybdate is added from the Reagent Feed System. The ammonium phosphomolybdate forms a precipitate that removes both cesium and cobalt from the extractant at low solution pH. The removal efficiencies for cesium and cobalt are 96% and 99%, respectively. The precipitate is eventually settled in the clarifier and is separated from the supernatant extractant.

Floc-Clarifier #2 - Extractant is pumped from the first floc-clarifier to this unit where pH adjustment with NaOH is accomplished. The 50% NaOH solution is added to the extractant to raise the pH of the liquid to 9.0 units. The increase in pH forms a metal hydroxide sludge thus removing many heavy metals, including chromium, from the extractant solution. Generated sludge is eventually settled out in the clarifier section of this unit operation, thus facilitating the separation of the sludge from supernatant.

Sludge Holding Tank - The sludge generated by the precipitation steps in the floc-clarifier is pumped to a sludge holding tank prior to dewatering.

Filter Press - The sludge from Floc-Clarifier #1 and #2 is dewatered by this unit operation. The dewatered sludge is sent to further processing not evaluated during the pilot study.

Filter Units - The extractant that has been ammonium phosphomolybdate treated and pH treated is final-filtered before being sent to an analyte sample station to remove residual suspended solids from the extractant. The flow from the sample station proceeds to the Treated Extractant Storage Tank.

Treated Extractant Storage Tank - Storage in this tank is the end unit operation for Scenarios #2 and #3. From this tank, the treated extractant would be recycled back to the treatment process or sent to ultimate disposal not addressed in this study.

Performance and Costs

The results of the mass balance sheet show that the assumed criteria for treated WWP sediment cesium concentration may not be achieved even by a two-staged acid extraction system. The two-staged nitric acid extraction system theoretically produces treated WWP sediment that has an average cesium concentration of 1,080 pCi/g, using WWP sediment with an average calculated cesium concentration of 9,802 pCi/g. However, if the treated sediment material is capped with clean fill as part of typical pond closure activities, compliance with the assumed criteria of 690 pCi/g average cesium concentration may become reality.

As part of the mass balance calculations performed, volumes and masses of process residues were defined. Table 4-8 includes information on residues that will ultimately require further processing or treatment.

A summary of the cost estimates for these scenarios are included in Table 4-9.

Table 4-8. Summary of estimated quantities of potential residues require further processing.

Residue	Scenario	Estimated secondary waste mass or Volume ^a
Untreated extractant	1	81,500 gal/day (16,300,000 total gal) to ICPP (if acceptable) ^b
NaOH sludge	2, 3	287,100 lb/day (28,710 total tons) (wet weight) to further processing ^c
Ammonium phosphomolybdate sludge	2	20,960 lb/day (2,096 total tons) (wet weight) to further processing ^c
Ion exchange resin	2	51,500 lb/day (5,150 total tons)
Filter media (sand, gravel, garnet, etc.)	2, 3	Not established during treatability study

a. Based on treatment of 103 yd³/day of WWP sediment.

b. Results of treatability testing indicate failure with ICPP WAC.

c. Typically a sludge dewatering unit would be employed to reduce both the weight and volume of sludge to be further processed.

Table 4-9. Preliminary treatment scenario cost estimates.

Scenario	Capital costs	Operation and maintenance costs	Total annual costs
#1 - ICPP	5,367,300	104,348,100	109,715,400
#2 - Ion Exchange	7,204,700	49,445,420	56,650,120
#3 - Chemical Precipitation/Complexation	7,267,300	75,326,400	82,593,700

A comparison of these cost estimates with the cost estimate presented in the ROD, shows that these cost estimates are significantly higher than the one in the ROD of approximately \$7,000,000. The primary reason for this cost difference is that the ROD cost estimate did not address extractant treatment and disposal and system operational factors such as labor, system monitoring, chemicals, safety considerations, etc. The greatest single cost item for each of the options is as follows:

- Option #1-ICPP: \$97.6 million for the cost of extractant treatment at ICPP
- Option #2-Ion Exchange: \$41 million for ion exchange resins
- Option #3-Chemical Precipitation/Complexation: \$64.5 million for ammonium phosphomolybdate

Each of these cost items has a very large cost impact on the respective option. By using recycle for nitric acid, the costs for disposal at ICPP (Option 1) may be significantly reduced. However, the effectiveness of acid recycle was not evaluated during the treatability studies. By using regeneration for the ion exchange resins, the resin costs for Option 2 may also significantly decrease. This potential has also not been evaluated, and in some cases of radioactive ion exchange treatment, disposal of regeneration waste streams is as costly as the resin costs. The costs for Option 3 may also be significantly reduced by optimizing the precipitation/complexation process and if the ammonium phosphomolybdate can be purchased in bulk quantities at bulk prices. At present, a bulk supplier for ammonium phosphomolybdate has not been located.

Although these cost items may be significantly reduced, the total cost for each option, including capital costs and other operational costs, still far exceeds the ROD estimate.

To place the expensive treatment costs into perspective, it is helpful to compare costs on a \$/ton basis. The \$/ton summary for the treatability study scenarios compared to the ROD costs and the cost for removing heavy metals from soils using a similar technology is shown in Table 4-10.

The costs for the three proposed options are so much higher than the assumed cost from the ROD and for a similar heavy metals removal because the heavy metals and ROD cases do not address some of the most expensive cost factors associated with the estimates. A more equalized estimate would involve comparison of costs for only the physical separation and acid extraction treatment phase as shown in Table 4-11.

As shown by the information presented above, the costs for the treatability scenarios are more comparable with the ROD cost when extractant treatment costs are not addressed. In fact, both ROD and treatment scenario costs are less than the cost to remove heavy metals from soil extracted from an independent cost estimate.

Basis for Facility Size and Flow Rates

The basis for the cost estimates presented in this report are as follows:

- Duration of sediment treatment: Operation one season (April to October, 8 months total)
- Operational Mode: 24 hours/day; 7 days/week
- Estimated days of operation: 200
- System downtime estimate: 20%

If the treatment schedule is condensed or if operational downtime is greater than 20%, system sizing would have to be increased to accommodate higher sediment throughput. Increased equipment size would ultimately increase the capital cost of the sediment treatment system.

Table 4-10. Comparison of total estimated costs.

Scenario	\$/Ton	Comment
ROD Cost	164	Does not include cost for extractant treatment or operational costs.
#1 - ICPP	2,493	Includes cost for extractant treatment and operational costs.
#2 - Ion Exchange	1,287	Includes cost for extractant treatment and operational costs.
#3 - Chemical Precipitation/Complexation	1,877	Includes cost for extractant treatment and operational costs.
Heavy Metals Removed ^a	400	Does not includes cost for extractant treatment or system operational costs.

a. R. Mayfield, *Evaluation of a Proposed Treatment Process to Reduce Heavy Metals Toxicity in Contaminated Soils and EAC Dust*, Golden Associated, (presented at Purdue Industrial Waste Conference, 1992.

Table 4-11. Cost comparison for physical separation and acid treatment.

Scenario	\$/Ton
ROD Cost	164
#1-ICPP	262
#2-Ion Exchange	262
#3-Chemical Precipitation	262
Heavy metals removed ^a	400

a. R. Mayfield, *Evaluation of a Proposed Treatment Process to Reduce Heavy Metals Toxicity in Contaminated Soils and EAC Dust*, Golden Associated, (presented at Purdue Industrial Waste Conference, 1992.

5. RESULTS OF THE SELECTIVE EXTRACTION TESTS

The Selective Extraction tests included initial sediment sample characterization, time-release profiles, and the sequential Selective Extractions. Results of these activities are presented in Sections 4 and 5 of Appendix B. The initial sample characterization is summarized in Section 3 of this report, and the time-release profiles and the sequential Selective Extractions are summarized in this section.

5.1 Time-Release Profiles

The duration of each extraction step outlined in the original plan was selected or estimated based on the available literature to ensure complete dissolution of the target matrix component. In conflict with this goal is the potential for contaminants to resorb to different types of sites on the solid residue during the extraction. This would produce a cascade of contaminant species from one type of site to another as the dominating fixation sites are destroyed by dissolution. If significant resorption occurs, no matter how selective or complete the extractions are, the natural contaminant distribution would be grossly misinterpreted.

To test this hypothesis, time-release studies of net radionuclide release were done with and without a potassium nitrate brine to inhibit the resorption of the cesium. Extraction solutions were analyzed after various selected exposure times to determine optimum conditions for cesium release in the carbonate, easily reducible and moderately reducible dissolutions. Cesium was tracked for the optimization because it is the dominant risk driver in the site risk analysis, and its strong γ -scan signature allows very sensitive monitoring of incremental changes over time. Potassium was chosen as the displacing ion because it is closest in size, charge, and chemistry to cesium, and therefore has the greatest potential for penetrating and displacing cesium from adsorption sites and/or preventing resorption. Based on these time-release studies, extraction times were selected for use in the subsequent sequential extractions to achieve maximum removal of cesium within the most reasonable extraction time.

The experiments indicated very rapid resorption of the cesium and cobalt, manifested in no gradual decline over time, but a significant decrease in the apparent initial release. In all cases the brine enhanced the net release of the extraction. The magnitude of the brine effect was substantially greater for cesium than cobalt, and much less for matrix constituents such as calcium, iron and manganese. This apparent selectivity may be attributed to two equally plausible causes: (a) potassium may, in fact, specifically displace cesium over cobalt, (b) cesium may simply have a greater tendency for resorption so its net release is affected more by any counter ion. Neither of these possibilities may be ruled out entirely by the data. However, some insight may be gained from the easily reducible extraction results. Assuming no synergistic effect on dissolution by the brine, the difference in release between the experiments with and without brine is the amount that resorbs. Noting that the brine produces a ten-fold increase in cesium release in the easily-reducible phase extraction, it can be concluded about 90% of the cesium can resorb under these conditions and only 10% of the extracted cesium stays in solution. This relationship does not hold for cobalt under the same conditions. The net release of cobalt without brine is 50-60% of the total available in the sample. Clearly less than 90% of the released cobalt resorbs. At parts-per-trillion levels, it is extremely unlikely that the adsorption capacity of the residual solid is limiting, therefore the tendency for cobalt resorption on the remaining sites must be less than that for cesium regardless of the selectivity of the brine. Thus, the magnitude of the brine effect is at least partially an indication of the degree of resorption on the remaining solid.

The brine had a significant effect in the carbonate extraction, shown in Figures 5-1 and 5-2. Net release of cobalt was increased by about a factor of two. Net release of cesium was increased by almost an order-of-magnitude. The required extraction duration to ensure carbonate destruction, however, was less well defined. With increasing extraction time, there was a gradual increase in calcium and radionuclide release over 1,080 minutes (18 hours), with no definite plateau indicating the completion of the carbonate dissolution. A longer term study to define the entire profile was then run for 48 hours. While there was still no obvious endpoint, the radionuclide levels did not increase appreciably beyond about 24 hours. In addition, elemental analyses of the residue and extract indicated about 80% destruction of the carbonate and increasing attack on manganese and iron phases. Thus, while it is conceivable additional decontamination could be accomplished using the carbonate extractant, the extraction time selected was 24 hours as a compromise between extraction efficiency and selectivity. Any residual carbonate is destroyed in later extractions.

The time-release profiles for the easily reducible phase extraction are shown in Figures 5-3 and 5-4. Extraction of the easily-reducible metal oxide phase, characterized primarily by oxides of manganese and noncrystalline iron oxides, appeared to be essentially complete in the first 3 to 4 hours based on the liquid-phase concentrations of these metals. Although the calcium release continues to increase beyond 18 hours, it does not track with the radionuclide release profiles, which plateau after about 18 hours (1,080 minutes). Again the brine enhances release, and the apparent effect is most pronounced for cesium (10x) as discussed above. Based on the radionuclide release profile, the extraction duration was increased to 18 hours.

The time-release profiles for the moderately reducible phase extraction are shown in Figures 5-5 and 5-6. The extraction profile for the moderately-reducible oxides, which should be essentially the crystalline oxides of iron, showed a continuous upward trend over 48 hours. Levels of manganese and calcium in solution continuously increased, but are not apparent because their concentrations are one to two orders-of-magnitude lower than the iron release. This confirms that the prior extractions were effective, as any residual calcium carbonate or manganese oxide would also be dissolved in this step. The radionuclides also showed a continuous release over the 48-hour time study. To maximize destruction of the phase, the extraction duration was increased 50% over the time-study period to 72 hours.

5.2 Mass Dissolution

Air-dried samples were weighed before and after each extraction to estimate the mass of the sediment dissolved in each step. Repeatedly transferring the material back and forth from centrifuge tubes (used for extraction, solids separation, and rinsing) to petri dishes (used to expedite drying) proved too cumbersome to provide reliable data. In addition, two samples were lost in the organic digestion step, when the concentrated peroxide extractant reacted violently with the high surface area samples containing about 2.5 Wt.% organic material. The remaining two samples indicated a cumulative weight loss of about 22 and 26 Wt.% over the five extractions. Observation suggests each determination might be 0.5 to 1.0 Wt.% high for a nominal weight loss of as much as 20 wt%.

Four samples were carried through the entire sequential extraction. In addition a virgin, previously untreated sample, was also extracted in each step. These untreated samples indicated the performance of each extraction step without interference from the other steps. A comparison of the data on a weight basis alone indicates comparable dissolution whether the sample was previously exposed or not, with the exception of the easily reducible extraction that dissolves about 50% more material from a virgin sample. Comparison on an elemental basis indicates that weight loss alone is not adequate to evaluate the selectivity of the extractions. In most cases, the virgin samples do

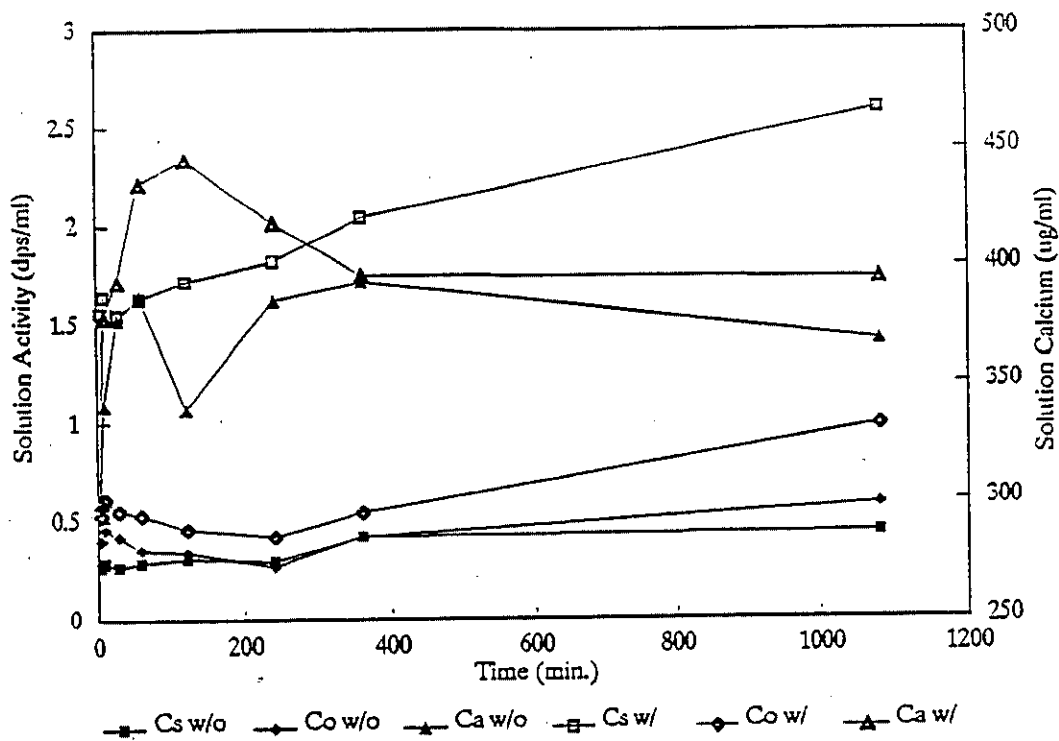


Figure 5-1. Time release profile for carbonate extraction with and without KNO_3 brine to control resorption.

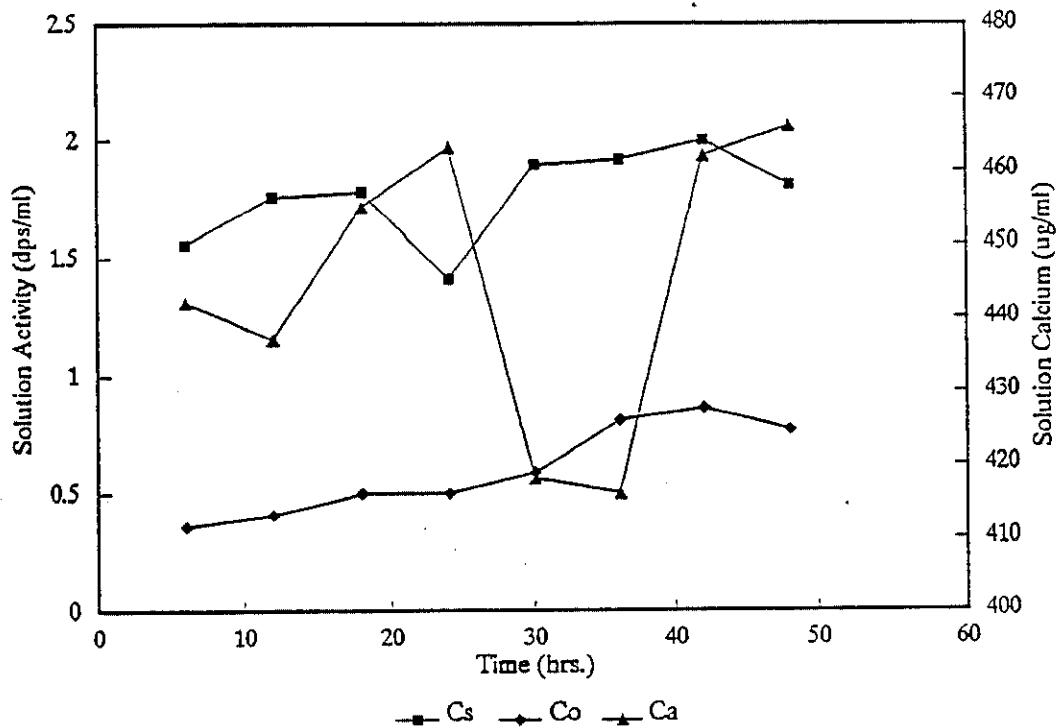


Figure 5-2. Extended time release profile for carbonate extraction with KNO_3 brine to control resorption.

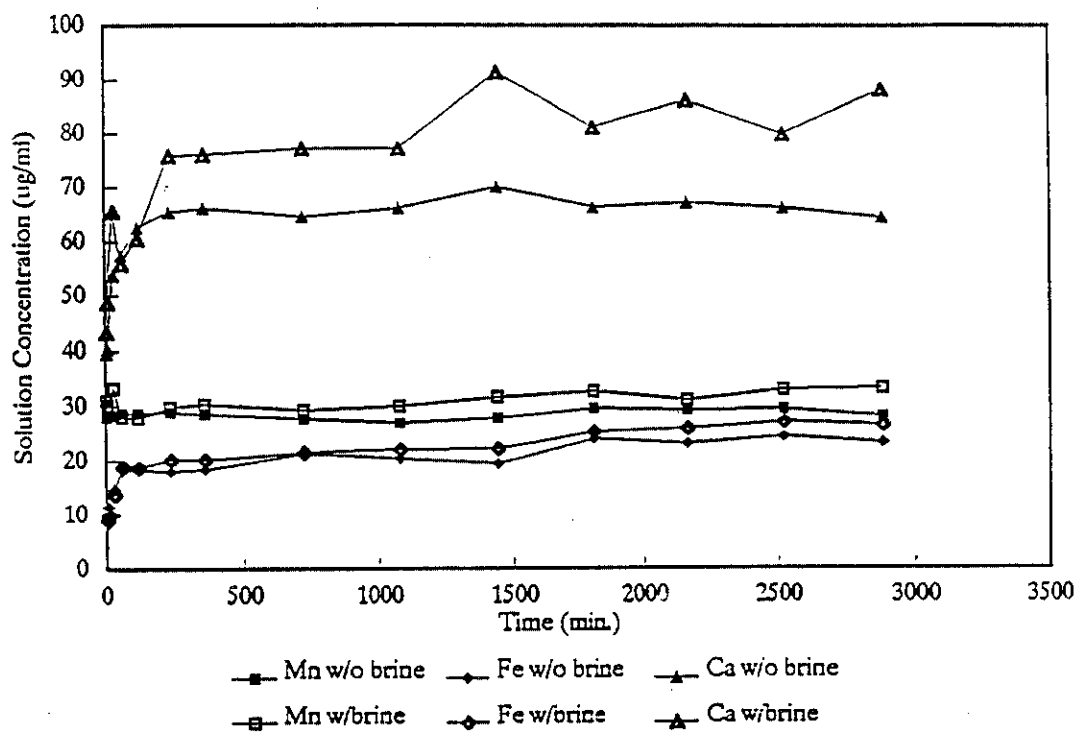


Figure 5-3. Elemental time release profile for easily-reducible phase extraction with and without KNO_3 brine to control resorption.

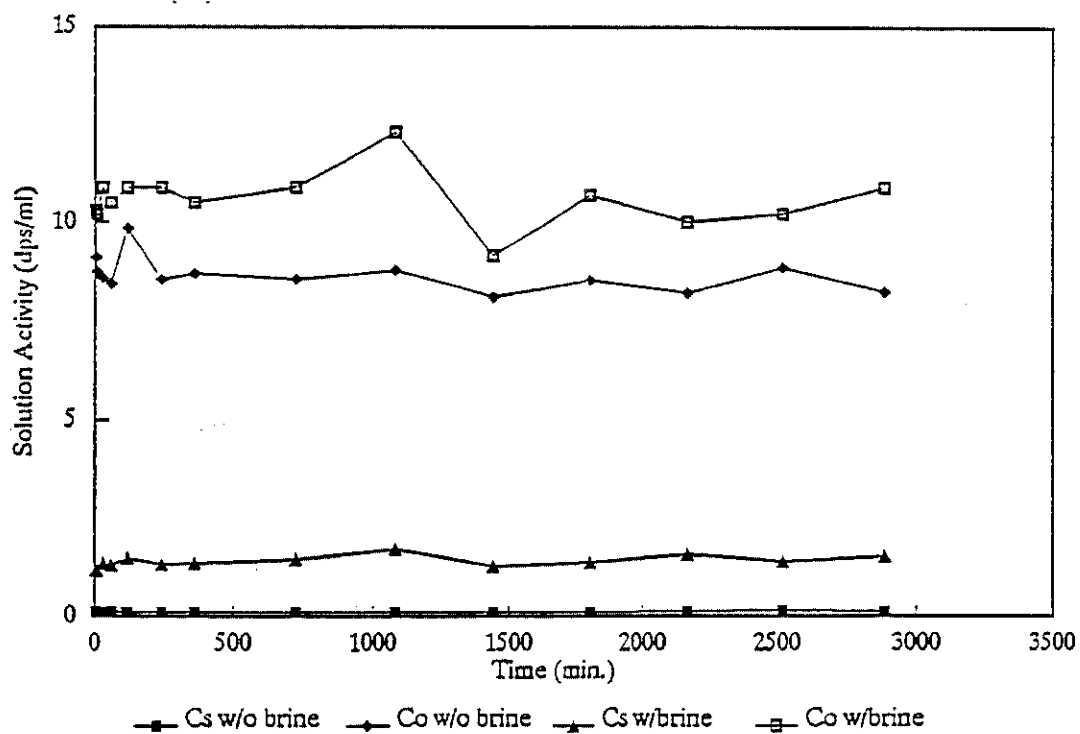


Figure 5-4. Radionuclide time release profile for easily-reducible phase extraction with and without KNO_3 brine to control resorption.

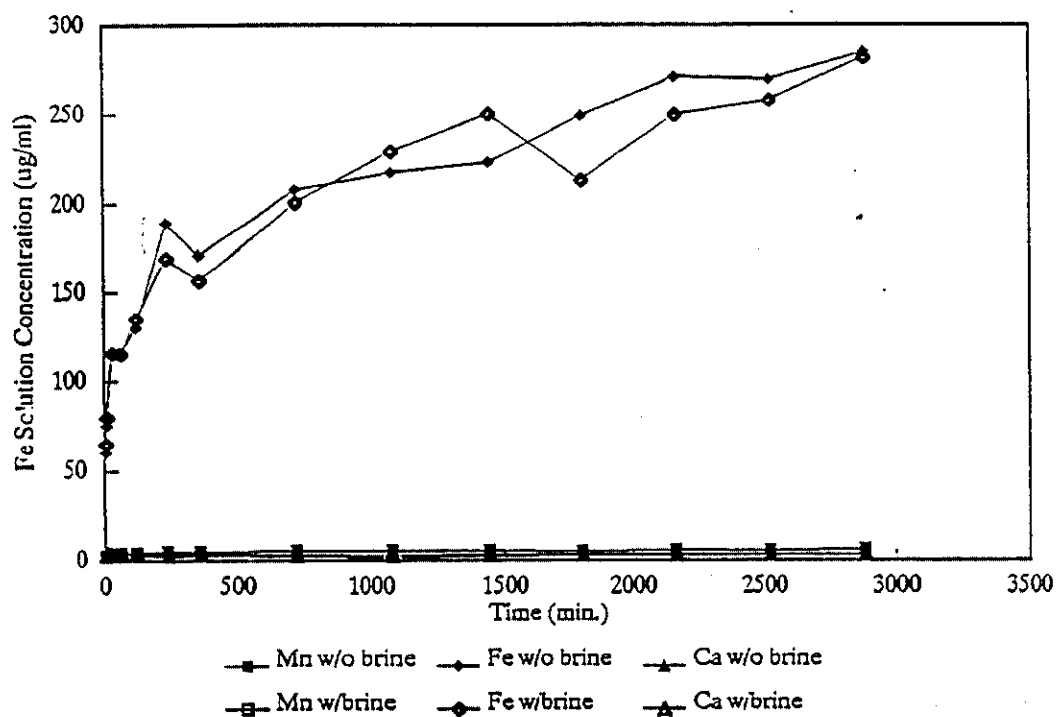


Figure 5-5. Elemental time release profile for easily-reducible phase extraction with and without KNO_3 brine to control resorption.

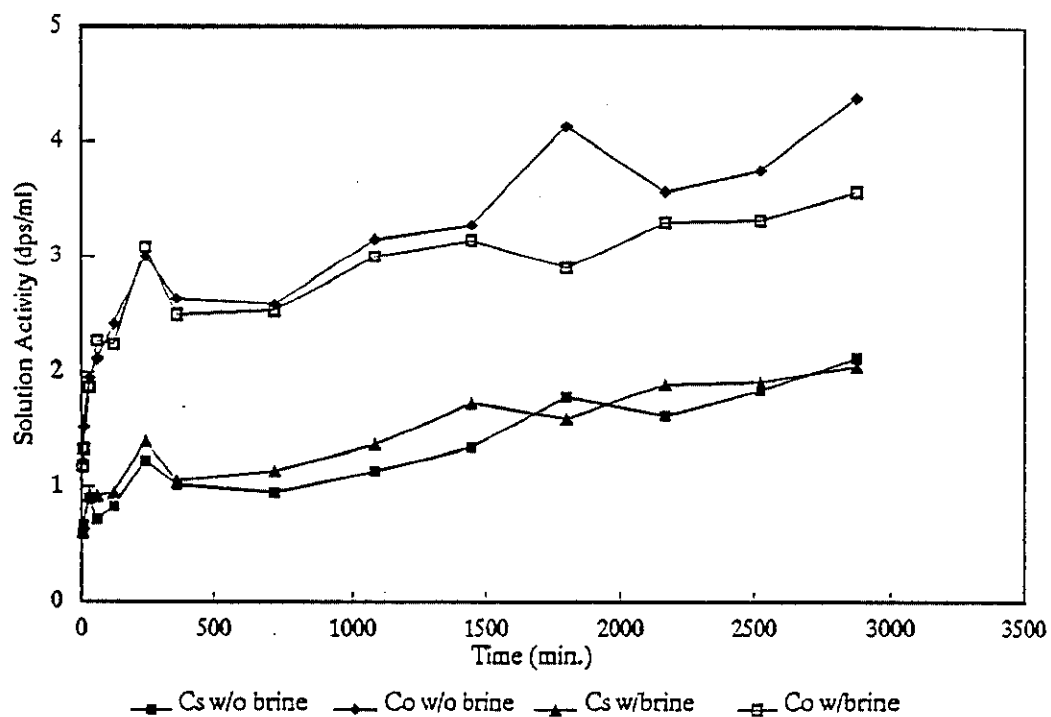


Figure 5-6. Radionuclide time release profile for easily-reducible phase extraction with and without KNO_3 brine to control resorption.

indeed yield more contamination than the previously extracted samples, indicating some nonspecific attack as the extractants become more corrosive. Ranges of sediment dissolution for each extraction are

- Ion exchange, 2–2.2 Wt.%
- Carbonate extraction, 4.6–4.7 Wt.%
- Easily reducible metal oxides, 4.3–6.6 Wt.%
- Moderately reducible metal oxides, 3.4–4.4 Wt.%
- Organic extraction, 3.7–3.7 Wt.%.

5.3 Radionuclide and Chromium Release

Radionuclide release in the extractions was essentially the same as that predicted by the time studies, confirming the reproducibility of data using this technique. Total cesium and cobalt release was 18% and 84%, respectively. The cesium and cobalt release in each sequential extraction is summarized in Figure 5-7 and 5-8. About half the total cesium released was by simple ion exchange, with the remainder distributed amongst the organic, iron oxide, carbonate, and manganese oxide phases in order of decreasing significance. Over three-quarters of the cobalt released was attributed to the manganese oxide phase, the balance distributed amongst the iron oxide, carbonate, and organic phases in order of decreasing significance. No cobalt was detected in solution following the ion-exchange step. Summing the released activity with that measured in the final residue dissolution, a mass closure of about 86% and 104% for cesium and cobalt, respectively, was obtained.

The small amount of silicon and aluminum found in the sequential extractants confirms the intended negligible attack on the lattice. Comparing these results to the reported 80% recovery of cesium in a preliminary evaluation of extraction with nitric acid, it can only be concluded that the nitric acid actually etches the underlying silicate mineral surface, partially digesting the mineral grain to release the adsorbed contamination.

Over 90% of the chromium in the sample is extractable. As shown in Figure 5-9, about 57% of the total chromium contamination in the sample is released from the iron oxide phase. The organic phase also contributes a significant fraction (21%), followed by the carbonate and manganese oxide phases, with no significant release in the ion exchange extraction. The mass closure on chromium was uniformly over 100% for all samples, indicating the initial analyses may have been low.

5.4 Extraction Specificity and Completeness

The extraction sequence was designed with progressively more aggressive chemistry with the understanding that succeeding steps would complete the dissolution of any residual material from a prior step as well as attacking the targeted phase. The ability of successive extractions to dissolve any remaining residual matter from prior phases was also observed in the results. The new (unexposed) samples typically released more contaminant than samples that were exposed to previous extractions because, in the new samples, the more easily removed phases were still present. However, in many cases the release from new samples was not as much as all prior steps combined, and in some cases, the previously exposed samples actually release more material than the new samples.

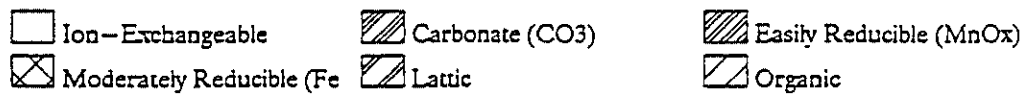
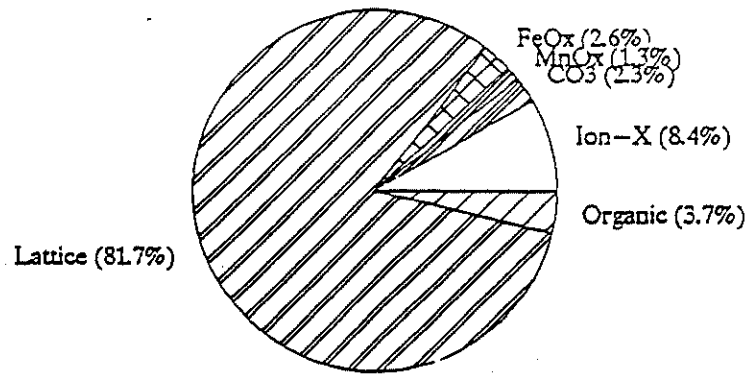


Figure 5-7. Cesium distribution by phase.

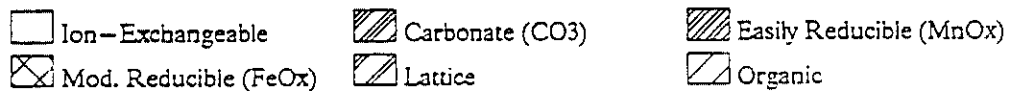
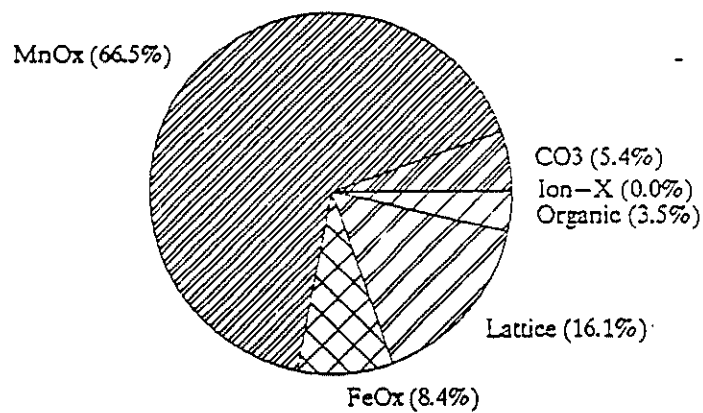


Figure 5-8. Cobalt distribution by phase.

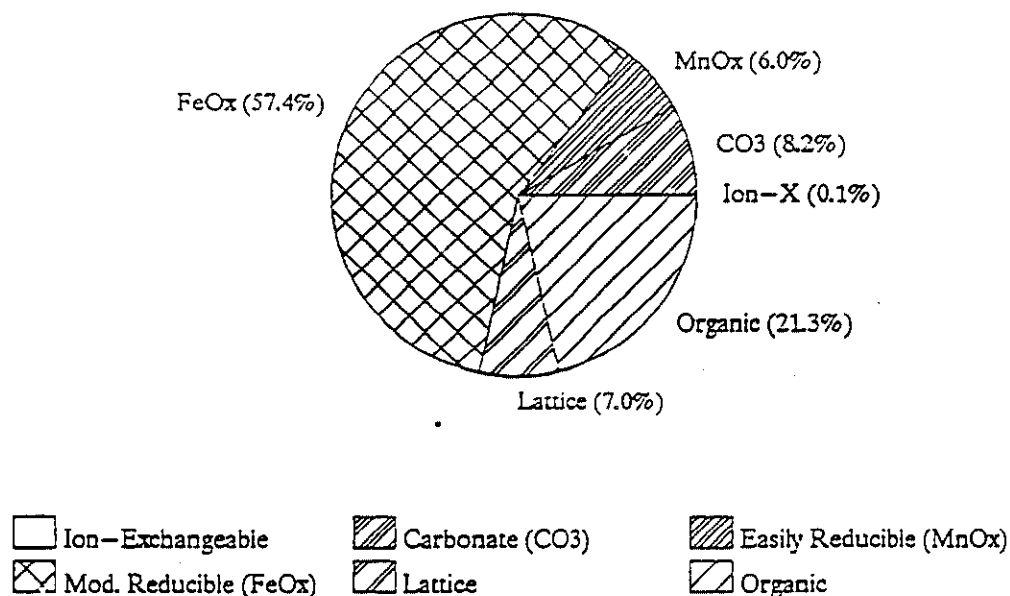


Figure 5-9. Chromium distribution by phase.

It appears that though there is large overlap between the carbonate, manganese, and iron extractions, there is some fraction of each phase specifically dissolved only by the intended extractant. This apparent chemical specificity may also be explained by the overlapping layers of the three phases and the sequence in which they are removed. The carbonate and metal oxide phases all form gradually over time due to mineral weathering. Possibly one extraction makes more of another phase available to a later extraction by removing a surface film or an intermixed phase (causing surface porosity).

The ion-exchange step not only provides the primary decontamination step for cesium, but also releases significant calcium (13%) from the matrix. This is due to partial dissolution of the carbonate phase in the ion exchange step because about 7% of the carbonate is also released into solution. No effect is apparent on chromium, cobalt, or any of the soil matrix constituents. These other metals are apparently bound as oxides rather than exchangeable ions.

The carbonate extraction only removes an additional 40% of the total calcium from the matrix, but the carbonate in the residue is diminished a further 80%. This is a good example of the difference between available material and that bound in the unweathered mineral. Only 10% of the carbonate is left in the sample, but close to half of the calcium is still bound. The remainder of the carbonate may well have been extractable, but as described in the time-release study, the extraction was terminated after 24 hours because of the attack indicated on the easily-reducible phase. About 30% of the total manganese (50% of the extractable content) was also dissolved. This release is attributed to lack of specificity, but some of the manganese may have been available in the carbonate phase rather than fixed to the underlying particle.

The manganese oxide and iron oxide extractions complete the release of available material from prior steps as expected. The manganese step frees little iron, and neither cause significant attack on the underlying mineral. As with the calcium, 70% of the iron and about 25% of the manganese is

left in the mineral residue. It is believed this material is contained in the intact mineral lattice, but the experimental data cannot verify complete dissolution of the surface deposit.

The organic digestion alone (containing brine) released about as much material as the organic and ion exchange steps in the sequential extraction combined. Little attack is indicated on any other phase. Calcium release is slightly greater, which may be due to the nonspecific attack or the natural calcium content in biological material. Reduced iron extraction for the extraction of new samples compared to the sequential results may be attributed to the diminished iron phase available due to covering by the other phases. Silicon and aluminum extraction is minimal, indicating negligible attack on the mineral matrix.

Analysis of the extraction residues was limited by sample variability. The dissolved residues were compared to complete digestions of unexposed samples to determine the percent dissolution in each step. The resulting number is therefore a calculated difference between two relatively large values with significant intrinsic variability. While the data is a good indication of gross effects (i.e., the manganese extraction residue confirmed over 60% cobalt decontamination, with dissolution of half of the calcium and three-quarters of the manganese), more minor effects are masked by the data and do not provide reliable confirmation of the extraction results.

6. CONCLUSIONS

Treatability studies were performed by the DOE to evaluate physical and chemical treatment of the sediment in the WWP at the TRA. The studies were performed at TCT and WINCO, using samples collected by EG&G Idaho. Sample characterization, including particle size distributions, radionuclide activity distributions, and elemental distributions were performed by both TCT and WINCO. WINCO also performed SEM and crystalline phase characterization of the samples. Acid Extraction, treatment of the extraction liquids, and preliminary conceptual design was evaluated by TCT. Selective Extraction of specific phases of the sediment, designed to identify and attack the specific mechanisms of contamination in the sediment, were performed by WINCO.

The overall conclusions from these studies are

- The larger sized particles have less contamination than smaller particles although none of the size fractions evaluated in these studies had cesium levels within the ROD goal of 690 pCi/g.
- At least 60 Wt.% of the sediment in the samples was in the +8 mesh size fraction.
- Acid Extraction using up to two stages does not satisfy the assumed ROD goal of 690 pCi/g for the average of cesium contamination in sediment backfilled to the pond.
- Only 18% of the cesium (in -40 mesh samples) is associated with phases in and on sediment particle coatings that can be removed by soil washing techniques less harsh than nitric acid. About 82% of the cesium is associated with the sediment particle lattice structure and can be removed only by partial or complete dissolution of the sediment particles.
- About 84% of the cobalt (in -40 mesh samples) is associated with phases in and on sediment particle coatings that can be removed by soil washing techniques less harsh than nitric acid. About 67% of the cobalt is associated with the easily reducible manganese oxide phase.
- About 93% of the chromium (in -40 mesh samples) is associated with phases in and on sediment particle coatings that can be removed by soil washing techniques less harsh than nitric acid. About 57% of the chromium is associated with the moderately reducible iron oxide phase.
- From a preliminary conceptual design of a combined physical separation and chemical treatment process for the sediment, estimated total costs are much higher than the \$7.2 million cost estimated in the ROD. In addition, the assumed goal in the ROD of less than 690 pCi/g for the average cesium activity for sediment returned to the pond cannot be met, unless (a) significant amounts of sediment are not returned to the pond, or (b) the averaging effect of clean covering soil is included with the backfilled sediment.
- The process of dissolution in hot nitric acid results in dissolution of 20% or more of the soil matrix. A full-scale treatment process will result in very significant radioactive and/or mixed waste streams requiring further treatment and/or managed waste disposal. Depending on the selected treatment scenario for the liquid extractant the wastes may include radioactive untreated extractant hydroxide sludges (a mixed waste), ammonium phosphomolybdate sludge (a mixed waste), or spent ion exchange resin (a radioactive waste).

These individual facts lead to a determination that these processes will (a) not meet the ROD assumptions concerning the efficiency of physical separation, (b) not meet the ROD-postulated return criteria of <690 pCi/g cesium-137, (c) not meet the remediation cost assumed in the ROD, and (d) result in large quantities of radioactive and/or mixed waste which will require extensive management. In short, physical separation/chemical treatment of soils contaminated with cesium-137, at the levels in the TRA WWP, is not currently feasible.

The test-specific conclusions and recommendations from these treatability studies are provided by TCT in Appendix A and by WINCO in Appendix B. These conclusions and recommendations are summarized in the following sections.

6.1 Acid Extraction

Conclusions generated from Phase A activities are as follows:

- Over 60 Wt.% of the total sediment is in the particle size fraction with particle size greater than 8 mesh. However, none of the tested size fractions, including the fraction with the largest particle size (+4 mesh) exhibited cesium activities below the assumed ROD goal of 690 pCi/g. The cesium activity for the +4 fraction averaged 3,825 pCi/g, and the smaller particles averaged higher cesium activities, up to 55,750 pCi/g for the -200 mesh fraction.
- The majority of the mass of the contaminants of concern is concentrated in the -8 mesh sediment fractions. Approximately 71% of the total cesium, and 89% of the total cobalt activity is concentrated in the -8 mesh sediment. Approximately 96% of the chromium and 86% of the total metals was found in the -8 mesh sediment. By performing a physical separation step and then sending the -8 mesh material to the nitric Acid Extraction process, most of the cesium, cobalt, and chromium in the pond will be exposed to nitric acid dissolution.
- Based upon observations made during Phase A sieving activities, some of the contamination in +4, +8 and +16 mesh sediment fractions may be attributed to dust adhering to the particle surfaces or some migration of the contaminants into rock and cobble pores. This conclusion is supported by the wet particle sizing results from WINCO (compared to dry particle sizing results from TCT). The wet sieving can tend to rinse away some of the adhering surface fines, containing high levels of contamination. The cesium and cobalt activities for the +4 fraction from wet sieving were 37% and 68% lower than the corresponding activities from dry sieving.
- The greatest concentrations of cesium, cobalt, and chromium is associated with the finer sediment particles (i.e., <200 mesh material).
- The untreated sediment samples are within TCLP limits.

Conclusions from the Phase B tests are as follows:

- Temperature had the greatest effect on the cesium removal efficiency. At 50, 70 and 95°C, the best removal efficiencies increased from 58 to 81% with increased temperature. At 1, 4, and 8-hour extraction times, the best removal efficiencies increased from 77 to 81% with increased time. For 3, 6, and 12 M acid, the best removal efficiencies increased from 79 to 81% with increased acid strength. The best cesium extraction left about 2,000 pCi/g in the sediments.

- From extractions performed under a variety of parametric conditions, it was determined that the optimum extraction was 8 hours long, used an acid molarity of 3 M, and used temperature of 95°C. When the extraction time was 8 hours, and the extraction temperature was 95°C, a 12 M acid extracted only marginally better than the 3 M acid. The difference in removal efficiency between the two extractions did not exceed what would be an acceptable experimental error. Therefore, the lower concentration of acid, 3 M, was used for further testing.
- Based on initial cesium activities of at least 22,000 pCi/g for the -8 mesh sediment, the two-stage extraction effectiveness (up to 91% cesium removal) is not sufficient to meet the assumed ROD goal of 690 pCi/g. A cesium removal efficiency of at least 97% is required to meet this goal.
- Sediment matrix dissolution in single-staged extraction was higher at 20–22% than the 8.5% value observed in prior studies. During second-staged extraction, 13% more sediment was dissolved, totalling as high as 32% for the combined extraction.

Conclusions from the Phase C tests include

- Extraction results from the Phase B tests were confirmed using larger sample sizes for better representativeness. The single-staged extraction effectiveness was slightly higher than from the Phase B tests—approximately 84% for cesium and 87% for cobalt. Sediment dissolution of 20% was similar to the Phase B result from single-staged extraction.
- For the higher cesium activity sediment samples, the extraction effectiveness was lower at 57% for cesium and 67% for cobalt. An increase in the initial cesium activity of 4.6 (460%) resulted in a decrease of the cesium removal efficiency by 35%.
- While pH adjustment of the extraction liquids significantly removes cobalt from the extractant, it less effectively removed cesium. A large amount of sludge was generated by pH adjustment.
- The extraction liquids do not meet ICPP WAC. After pH adjustment to 9 and precipitation of dissolved materials, the liquid still does not meet ICPP WAC.

Conclusions from the Phase D tests include

- The ion exchange resin cesium-100 showed the ability to remove significant amounts of cobalt and cesium when used at very high dose rates. A dose rate of 70 g of resin per liter of extractant removed 67% of the cesium and 99% of the cobalt from the extractant.
- Chemical precipitation using ammonium phosphomolybdate demonstrated the ability to very effectively remove cobalt and cesium from the extractant. Cesium removal was 96% and cobalt removal was 99%.
- Reverse osmosis proved to be ineffective at removing contaminants from the extractant.
- No technology displayed the ability to produce an effluent meeting the ICPP WAC.

6.2 Selective Extraction

Conclusions from the Selective Extraction study include

- Results of the sediment sample characterizations tended to agree with the characterization results from TCT.
- Over 90% of the chromium can be extracted. Most of the cobalt can also be removed (84%), but with a half-life of only 5.271 years, a comparable reduction occurs naturally in less than 15 years. Cesium cannot be appreciably removed from the -40 mesh material by any practical soil washing because over 80% of the material (32,000 pCi/g in the -40 mesh sample) is bound in the silicate lattice.
- The sequential extractions verify that significant recovery of available species can be achieved with less aggressive chemistry than boiling acid. This technique can also provide an accurate account of contaminant distribution, with mass balances well within the precision of the soil matrix sample homogeneity. Confirmation of extraction completeness should be augmented by data other than simple residue analysis, possibly with SEM.
- Time studies to determine the required durations for extractions for a particular sample were essential. The times used were significantly longer than those reported in the literature. These studies also allowed identification of extraction complexities such as the procedure for conducting the organic digestion.
- The x-ray diffraction analysis indicated gross amounts of quartz (up to 50% of the crystalline species), with significant fractions of calcium carbonate and calcium and potassium aluminosilicates (feldspars). Lesser amounts of the oxides of manganese and iron were indicated (0-6 Wt.%), but the distribution of cesium, cobalt, and chromium by particle size had an apparent correlation with the incidence of these metals. Organic carbon content ranged from less than 1 Wt.% in the large material, up to almost 4.5 Wt.% in the fines, also showing a strong parallel to the contaminant distribution.
- Time-release profiles developed for cesium during the carbonate, manganese, and iron extractions showed a strong tendency for rapid resorption. Tests with and without a potassium brine present to inhibit cesium resorption indicated extraction efficiency could be enhanced by as much as a factor of ten using the brine. Potassium was chosen for its chemical and physical similarities to cesium. This selectivity was apparent in the extraction results that showed a much stronger effect on the cesium than on the cobalt.
- Soil washing by selective, chemical extraction cannot be practically applied to the TRA WWP sediments for cesium decontamination.

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Attachment A

Response to IDHW and EPA Comments to the Draft Treatability Studies Report

Attachment A

Response to IDHW and EPA Comments to the Draft Treatability Studies Report

IDHW COMMENTS

1. *The Draft Treatability Study report does a fairly good job showing that the cesium concentrations in the Warm Waste Pond sediment cannot be treated to below the ROD goal of 690 pCi/g in 60% of the sediments, except for the acid wash treatment method. IDHW/DEQ is concerned that physical separation treatment methods were not examined in as great a detail as the chemical separation methods in this study. As early information became available on the relatively poor performance of the chemical treatment tests in late July 1992, IDHW/DEQ suggested various physical separation processes (i.e., abrasion studies) needed to be evaluated. It was IDHW/DEQ's position at the time that the physical separation techniques separately and in combination with chemical extraction techniques needed to be tested and evaluated in order to determine the maximum efficiencies that could be achieved to meet the ROD goals in the study. This was not evaluated in the treatability study, thus it remains an important gap in the evaluation of cesium contaminated sediments of this type at the INEL and other DOE sites.*

Response:

The DOE is planning to pursue treatability studies for contaminated sediments, soils, and other sites at the INEL, even though further WWP treatability studies are not currently planned. Chemical and physical treatments will continue to be evaluated for treating other areas at the INEL that are contaminated with radionuclides such as cobalt-60 and cesium-137. At other sites, the contaminants may be affixed to soils by different mechanisms and may prove more amenable to physical separation or chemical treatment.

The DOE has performed studies, both in the laboratory, and theoretical, on the potential for physical separation techniques to be successful on sediments from the TRA WWP. Testing has been performed at the University of Utah and is reported in *Particle Characterization of Contaminated Soil* (J. D. Miller, May 1991), where physical properties such as size and density were determined. In addition, the soils were tested for electrophoretic mobility and magnetic separation. Many physical investigative techniques were used. They include scanning electron microscopy, X-ray diffraction, energy-dispersive X-ray fluorescence, and fourier-transform infra-red spectroscopy. All investigations indicated that the physical and chemical processes evaluated in the treatability studies could not practically meet the goals of the Interim Action ROD.

The DOE has also commissioned an investigation by NRT Corporation. NRT used a successive process of screening, sieving, and treating various soil fractions. Treatment techniques included soil washing with various chemical solutions, including nitric acid. Physical abrasion processes tested by NRT were not sufficiently effective. Nitric acid washing of some soil fractions showed marginal success in one case, but no success in other fractions. The case where acid washing met the desired cesium activity level was for a sediment sample that had a much lower initial cesium activity level (2,470 pCi/g) than the average of 9,805 pCi/g observed for the more representative samples used in the nitric acid extraction tests performed at TCT. NRT also performed testing using

attrition scrubbing to remove soil coatings and surfaces. Attrition scrubbing proved insufficiently effective meeting ROD goals.

Other types of physical abrasion treatments were investigated. The process of physical abrasion has been proven, in other situations, to remove only the top-most surface layers of sediments. More aggressive approaches, such as milling and rolling, cleave the soil particles along natural faults or crystal lattices and do not remove surface layers. Both of these methods are believed to have little, or no, applicability to contaminants in the WWP.

Making the assumption that physical processing might be successful in meeting ROD goals, DOE estimates that as much as 10% of the pond sediments would require long-term management as radioactive waste. This estimated volume translates into approximately 2,000 yd³, or about 7,400 drums. The sheer volume of waste material, in the opinion of the DOE, makes this option untenable due to long-term management costs,

2. *In reviewing the various acid extraction scenarios, the digestion and/or contact times of up to eight hours are protracted beyond reasonable treatment times for the scale up of a project of this nature (see Volume I, page 4-1). For the anticipated quantity of contaminated soils to be treated (22,000 yd³), the time required to treat the soils in the three ponds would be in excess of four years.*

Response:

The efficiency of the acid extraction time for these sediments depends on the extraction time, the acid type and molarity, and the extraction temperature. During Phase B of the acid extraction tests, the efficiency of nitric acid extraction for different extraction times between 1-8 hours, acid molarities between 3-12 M, and extraction temperatures between 50-95°C were parametrically evaluated. Separate aliquots of -8 mesh sediment samples were extracted using different extraction times, acid molarities, and extraction temperatures. The results of these parametric screening tests were used to determine the optimum extraction conditions for more detailed evaluation in the subsequent phases of the acid extraction test program.

The results of the parametric screening tests are shown in Volume I, pages 4-2 and 4-3 for cesium and cobalt removal efficiency. Cesium removal efficiency was the primary measure against which the different parametric conditions were evaluated, since cesium was the primary risk driver and since cesium was more difficult to remove than cobalt. As can be expected, the cesium removal efficiency tended to increase with increasing extraction time, extraction acid molarity, and extraction time. The highest cesium removal efficiency was 80.5%, obtained for the 8 hour, 12 M and 95°C test condition. The removal efficiency for the 12 M extractions decreased only slightly for the 4-hour and 8-hour extractions, as long as the temperature was maintained at 95°C. Furthermore, the removal efficiency for the 8-hour extractions was also consistently high as long as the temperature was maintained at 95°C. Lower temperatures resulted in significantly lower removal efficiencies regardless of the extraction time or acid molarity. Within the range of test conditions, relatively high cesium removal can only be achieved with either a long extraction time or with high acid molarity, or both.

From the perspective of full-scale treatment equipment and operations, conditions of high acid molarity and high temperatures tend to be more corrosive to equipment and hazardous to operator safety. Longer extraction times result in increased process equipment sizes (and capital cost) for longer retention times. However, MK Ferguson suggested that the most critical of these qualitative considerations may be the acid molarity (Personal communication from P. Rekemeyer, MK-Ferguson,

Boise, ID, to N. R. Soelberg, EG&G Idaho, Inc., Idaho Falls, ID, October 21, 1992). On this qualitative basis, the extraction conditions of 8 hours, 3 M and 95°C was selected for further testing. This selection was made following review with EPA and IDHW prior to continued tests.

It is true that an 8-hour extraction time was relatively long. Indeed, a shorter extraction time of 4 hours or even 1 hour also resulted in relatively high removal efficiencies, but only when the acid molarity was increased and the high extraction temperature was maintained. With respect to full scale operations, the longer extraction time was considered the "lesser of two evils" when compared to the acid molarity, especially under such high-temperature conditions.

The 8-hour extraction time was included in the design of the preliminary acid extraction process. In accordance with the specifications in the ROD, the preliminary acid extraction process was designed to treat all of the -8 mesh pond sediment within a 1-year duration. In fact, it was assumed that the treatment process could not take place during winter months. The duration of the treatment process was limited to 8 months within one operational season (Volume I, page 4-16).

3. *The generation of additional wastes (i.e., hard to manage waste sludges) through the type of acid dissolution performed on the soil matrix presents an unacceptable waste management problem.*

Response:

The DOE agrees with this comment.

4. *The statement on page 6-4, Volume 1 that "Soil washing cannot be practically applied to the TRA WWP sediments for cesium decontamination" has not been demonstrated fully with respect to the criteria listed in the ROD. It is IDHW/DEQ's position that sufficient physical studies as suggested in meetings in July 1992 were not performed. The treatability studies would have benefited from a physical separation standpoint had they been patterned after the paper on "Characterization Protocol for Radioactive Contaminated Soils" published in May 1992 by the U.S. EPA OSWER. This was provided to DOE-ID for consideration by IDHW/DEQ and EPA in August 1992.*

Response:

The term "soil washing" most commonly refers to washing with water, without chemical additives, to remove surface contamination by suspension and dissolution into the water. However, the term "soil washing" is used in the WINCO sequential selective extraction study (Vol. II, Appendix B) to refer to the process of extractions using increasingly harsh extraction solutions to selectively, chemically attack different mineral deposits within the sediment particles and on the particle surfaces. By this definition, soil washing was considered a chemical treatment rather than a physical treatment. The soil washing statement on page 6-4 has been changed to read "Soil washing by selective, chemical extraction cannot be practically applied to the TRA WWP sediments for cesium contamination."

The treatability study was designed to evaluate physical and chemical treatment of the pond sediments to meet ROD goals. The physical treatment used was physical separation. Physical separation was included in the test plan under the common assumption that the bulk of the sediment might be effectively decontaminated by removing smaller particles that contain relatively large amounts of contamination. Chemical treatment was considered the most likely treatment process for

decontaminating the smaller particles. Chemical treatment is typically considered more effective than simple soil washing with water for most decontamination processes.

Physical separation for decontaminating the bulk of the sediment was found to be unsuccessful in meeting ROD goals (Volume I, Section 3.2). Even the fraction with the largest particle size, +4 mesh (>4.75 mm), did not meet the ROD goal for cesium levels of less than 690 pCi/g. The particle size separation performed by WINCO was performed with a water wash. This was analogous to water washing, since the water was continuously sprayed over the sediment during gently agitated sieving. Analysis of the wash water following the sieving process showed that less than 0.1% of the analytes, including cesium, cobalt, and chromium, were removed in the water wash.

The treatability studies test plan was evaluated with respect to the paper on "Characterization Protocol for Radioactive Contaminated Soils" published in May 1992 by the U.S. EPA OSWER. The test plan was also discussed with EPA OSWER (Personal communication from M. Eagle, EPA OSWER, Cincinnati, OH, to D. Gombert, WINCO, Idaho Falls, ID, 1992).

5. *The section in Volume I: Main report entitled "Conclusions and Recommendations" does not contain any recommendations for further work. Certainly the performance of the aforementioned physical separations/techniques need further work and should be discussed in this section with respect to the potential benefits to other sites at INEL.*

Response:

The title of this section was renamed "Conclusions," and includes only the conclusions from the treatability studies. Recommendations are not within the scope of this document. For example, other recommendations such as preparing an Explanation of Significant Differences (ESD) and recommending consolidation/backfill of the pond sediment were also not included in this report.

6. *IDHW/DEQ questions why the NRT Corporation report entitled "Warm Waste Pond Bench-Scale Treatability Study" dated September 1992, was not considered for inclusion in the subject Treatability Study Report.*

Response:

The report by the NRT Corporation was not included in the Treatability Study Report because it was not identified in the Treatability Study Work Plan. It was a separate study, undertaken at the direction of DOE, in addition to the formal Work Plan. The NRT report has already been referenced in the subject Treatability Study Report. The NRT report has also been included in the Administrative Record.

EPA COMMENTS

1. *The data provided by TCT's acid washing studies show a clear positive relationship between increased cesium removal and an increase in nitric acid concentration, temperature, and time. The conclusion that the optimum treatment scheme is to use a lower 3 M nitric acid concentration, balanced by a higher temperature (95°C), and a longer extraction time (8 hours) is supported by the data. This procedure generates wastes of lower acidity than 6 M or 12 M extraction. Using the optimum conditions, the data show that approximately 80% of the cesium can be removed in a single wash, and 90% in a double wash.*

Response:

The DOE agrees with this assessment. Rounded to the nearest 10%, the values of 80% and 90% are accurate for the cesium removal efficiencies from single and two-stage extraction using 3 M nitric acid at 95°C for 8 hours.

2. *The study incorrectly concludes that this treatment technology is inadequate to meet the ROD goal of reducing the cesium concentration to below 690 pCi/g in 60% of the sediments. The study only considered size separation as a gross first step to remove the coarse fractions, with acid wash treatment applied only to the fines. An alternative treatment scheme would be double-stage acid washing of only the coarse fraction above the number 50 mesh (which makes up approximately 91% of the sediment volume according to Table 3-2, page 3-3). With this method, it appears possible that approximately 60% of the soil could be reduced to an average cesium activity of 690 pCi/g. This includes losses for matrix dissolution in a double acid wash treatment system. The fines have already functioned as a natural sorption medium and their removal can be viewed as a pretreatment step for removal of the most highly contaminated sediments, leaving treatable soils behind. However, the net result of such a treatment process could be that the volume of waste sludge generated from using chemical complexing agents, pH adjustment, or resin beads could equal or exceed the volume of soil cleaned by screening, creating no net advantage. The sludge could be even more difficult to dewater and dispose of than untreated soil. If soil washing is to be rejected, it should not be for the reason stated in the study. Instead, the study should include a mass balance to determine the final amount of contaminated solids requiring disposal.*

Response:

The objectives in the test plan included reducing the volume of the contaminated material by screening by at least 60%. This was to be done by separating the larger sized material that was less contaminated than the fines. If the larger sized material met the goal of 690 pCi/g or less, then it could be backfilled to the pond, while the more highly contaminated fines should be chemically treated. However, the test results showed that the contamination levels of the larger sized material exceeded 690 pCi/g, so the goal of at least 60% volume reduction by simple screening could not be met. Furthermore, the goal of an average cesium concentration of less than 690 pCi/g could not be met for either the large-sized fraction or the fines by size separation.

As suggested in the comment, it may be possible that the coarse material rather than the fines may be chemically treated to meet the ROD goal of 690 pCi/g for the coarse material. This scenario is shown in the flowchart of Figure 1. The numbers and calculations shown in Figure 1 are similar to the number and calculations used by the EPA for this comment. By physical separation, approximately 92% of the total sediment can be physically separated in the +50 mesh fraction for nitric acid extraction (Volume I, page 3-3). The average cesium concentration for this fraction would be around 6,920 pCi/g calculated using the activity data in Volume 1, page 3-3. The remaining 8% of the total material would have a cesium level of around 43,000 pCi/g, and could not be treated by reasonable means to reduce this level to less than 690 pCi/g. This material, amounting to about 1,700 yd³ (6,100 55-gal drums), would require long-term management. This condition alone represents a highly costly and undesirable disposal situation.

Using a best reasonable case scenario and using potassium nitrate to obtain an estimated higher removal efficiency (see EPA comment No. 12), perhaps only one extraction step may be necessary to achieve the necessary cesium reduction to achieve 690 pCi/g for the solid residue. Also

44,000 tons WWP Sediment
20,700 cy WWP sediment -->

+50 Mesh
Screen

+50 Mesh Sediment
From Vol. I. p. 3-3:
Wt.% = $57.94 + 11.21 + 8.41 + 14.45 = 92.01\%$
Volume = $0.9201 \times 20,700 \text{ cy} = 19,046 \text{ cy}$
Activity = 6.920 pCi/g

-->

Nitric Acid Unit
o 3M, HNO_3 , 8 Hrs
o KNO_3 addition
o Single stage
o Cs removal efficiency of $90\%^1$

-->

Thickener Unit
(Separation from
extraction)

-->

Extractant to Recycle
or
Treatment/Processing²
Dewatering/Filtration
Unit (Removal of
sludge from extractant)

-->

10% Sediment Dissolution
Sludge ppt = $(0.10) 19,046 \text{ cy} = 1,904.6$
Drums = $\frac{1,904 \text{ cy}}{0.27 \text{ cy/drum}}$
= 7,052 drums

↓

Long Term
Managed
Disposal
7,054 Drums

-50 Mesh Sediment
From Vol. I. p. 3-3:
Wt. % = $4.89 + 1.56 + 1.54 = 7.99\%$ of total sediment
Volume = $0.0799 \times 20,700 \text{ cy} = 1,653.93 \text{ cy}$
Activity = $\frac{0.0489 (38,150) + 0.0156 (45,800) + 0.0154 (55,750)}{0.0799}$
= 43,040 pCi/g
Drums = $1,653.93 \left(\frac{1 \text{ drum}}{0.27 \text{ cy}} \right) = 6,125.66 \text{ drums}$

↓

Long Term
Managed
Disposal
6,126 Drums

Extracted Residue
Volume = $0.90 (19,046 \text{ cy}) = 17,141.4$
Activity = $\frac{0.09 (6.920)}{0.90} = 692 \text{ pCi/g}$

↓

Return to Pond
Meets ROD Goals

¹The Cs removal efficiency is assumed, but based upon treatability testing on the sediment fines.
²This diagram does not address the treatment or processing which may be required if the % recycling of extractant is low or it technically is not feasible with respect to consistent Cs removal efficiency.

TCT
St. Louis

SIMPLIFIED PROCESS FLOW AND MASS BALANCE
DIAGRAM FOR WWP SEDIMENT TREATMENT SYSTEM
COURSE SEDIMENT SCENARIO

Figure 1

Project No.	9252-2000
Drawn By:	AK
Chk'd By:	RAB
Date:	4/13/93

assuming best case for a single-stage extraction, sediment dissolution may be as low as 10% (from Vol. I, page 4-4, Phase B dissolution was 22%, Phase C dissolution was 20%, and dissolution from earlier bench-scale tests was 8.5%). The remaining treated residue would be around 17,000 yd³, and the dissolved sediment would be around 1,900 yd³. Most of this dissolved material would be precipitated out of solution to enable the supernatant to meet ICPP acceptance criteria for calcination. The precipitated sludge, up to 1,900 yd³ (7,100 drums), would require long-term management. This condition also represents a highly costly and undesirable disposal situation. Together with the 6,100 drums of untreated fines, up to 13,200 drums would require long-term management.

The treated residue will meet the ROD goal of 690 pCi/g if the removal efficiency of the extraction process is 91% of the initial cesium, accounting for the 10% assumed dissolution of the sediment. Also, the treated residue will comprise around 83% of the total sediment, and it can be returned to the pond. The remaining 17% of the sediment represented by the untreated fines and the sludge would be highly contaminated.

The size of the extraction facility would have to be around 3 times higher than the preconceptual design described in Volume I, Section 4.4, if the treatment is to be performed in the same timeframe. This would significantly increase facility capital cost. Even if the treatment time were extended, the demand (and cost) for treatment chemicals including nitric acid and sodium hydroxide would be approximately 3 times higher. The cost of potassium nitrate would also be added, since it was not included in the original preliminary design. Depending on the extractant treatment option, there would also be increased demand and costs for other chemicals and reagents including ammonium phosphomolybdate (for precipitation/complexation), filter media or ion exchange resins. The increased chemical demand would add many millions of dollars to the cost of the treatment process.

By varying the proportions of treated sediment and untreated fines (by changing the mesh size of the separation process), the relative proportions will change. Decreasing the amount of the treated material would enable easier and less costly acid extraction, but the amount of untreated fines for long-term management would increase. If the amount of treated material is increased by including more of the fines, the amount of untreated fines would decrease, but the extraction would become more difficult and costly, the percentage and amount of sediment dissolution would increase, and the amount of sludge would increase. These increases would counterbalance the benefit of reduced untreated fines.

In summary, this type of treatment scenario might optimistically meet the ROD goal of 690 pCi/g cesium concentration for around 83% of the sediment. However, the remaining 17% (3,500 yd³ or 13,200 drums) of the sediment would consist of fines and sludge material and would be highly contaminated with cesium, on the order of 43,000 pCi/g for the untreated fines. The sludge would also be highly contaminated. The ROD goal of an average cesium contamination level of 690 pCi/g would not be met, and large volumes of highly contaminated fines and sludge would require long-term management in a facility that does not presently exist. This treatment scenario does not suitably treat the entire pond sediment as a whole because the fines are left highly contaminated. The ROD goals apply to the entire sediment, not to only a portion of the sediment.

3. *It is likely that the addition of potassium nitrate to the optimum acid wash treatment selected in the WINCO study would also significantly increase the efficiency of the acid wash system.*

Response:

While it is clear that addition of potassium nitrate to sequential extraction solutions enhanced dissolution of cesium by a factor of 2-8, there is no data supporting, or contradicting the postulation of enhanced removal effectiveness with nitric acid. Using potassium nitrate to enhance acid extraction was not tested. However, there is a key difference between the observed performance of potassium nitrate during the sequential extractions compared to the potential performance during the nitric acid extractions. For the sequential extractions, the cesium dissolution that was enhanced was the cesium associated with the relatively easily removed surface deposits, which was only 18% of the total cesium. The nitric acid extractions attack not only the easily removed cesium, but also the more difficult to remove cesium in the crystal lattice structure of the particles. It is not known how effective the addition of potassium nitrate would be for the extraction of the cesium bound in the crystal lattice. The examination of assumptions, accompanied by a mass-balance, is shown in the response to EPA Comment No. 2. This evaluation has shown that the associated waste management problems, even with enhanced removal effectiveness, makes this approach prohibitive in nature.

4. *Volume 1, Section 2.2.2.6 - This section specifies a final lattice phase digest with hydrochloric and nitric acid at 50°C. It is not clear what the results of this step were.*

Response:

The purpose of total digestion was to obtain an accurate measure of the chromium, cobalt-60 and cesium-137 contaminants remaining in the crystal lattice structure of the sediment particles following removal of the more easily extracted surface deposits. These determinations allowed an accurate mass balance of contaminants for each of the selective extraction stages. This paragraph of the report has been clarified.

5. Appendix B, Section 4.6, paragraph 2

Please clarify how this information relates to representative samples.

Response:

The content of this paragraph on page 41 describes the data in Table V (on the same page, and called out in paragraph 1 of Section 4.6). The cesium, cobalt, and total γ -activities are reported in pCi/g. The paragraph is describing to the reader how to use the cesium and cobalt half-lives to determine their elemental concentrations in parts per billion and parts per trillion. By weight, there is 0.48 parts per billion cesium and 8.24 parts per trillion cobalt, compared to 3,135 parts per million chromium. Using atomic weights, there is about 25 times as many cesium atoms as cobalt atoms in the sample. This paragraph of the report has been clarified.

6. Appendix B, Section 6.0, Conclusions and 7.0 Recommendations

Conclusions and recommendations are not fully supported by the research conducted. The purpose of this Appendix should be to present results of the research conducted and not opinions of the document preparer. Several statements concerning half lives and natural decay, plant uptake and this technology not being "practical," should be clarified and supported by the research.

Response:

Paragraph 1 of Section 6.0 on page 59 have been edited to remove discussion about the decay of cobalt and the stability of cesium bound in the sediment silicate lattice. However, these points are relevant, because the results of the study showed that (a) about 84% of the cobalt could be removed by chemical treatments less harsh than hot mineral acid extraction, but (b) cesium contamination could not be effectively removed by similar chemical treatments because over 80% of the cesium was bound in the silicate lattice. Considering the cobalt alone, a reduction comparable to 84% can be obtained by doing nothing and letting the cobalt naturally decay in less than 15 years. Considering the cesium alone, the results of the study show that a variety of chemical treatments cannot leach the cesium from the silicate lattice. It can be speculated that this cesium is well immobilized in the silicate lattice, and relatively impervious to groundwater leaching or mass transfer and uptake by plant roots.

Section 7.0, Recommendations, has been deleted from Appendix B.

7. Acid Wash Extractant and ICPP WAC

Data from the report show that acid wash extractant would not meet the ICPP WAC. None of the treatment technologies tested was able to clean the extractant enough to satisfy ICPP WAC. However, complexation with ammonium phosphomolybdate followed by pH adjustment successfully removed most of the ICPP WAC constituents. It is possible that further treatment could allow the extractant to meet the ICPP WAC.

Response:

As reported in Volume I, page 4-9, the complexation tests showed effective removal of 96% of the cesium and 99% of the cobalt in acid extraction solutions. The supernatant exceeded the ICPP WAC limits for arsenic and sulfate, and the pH was too high. According to Table 4-6 (page 4-12), the arsenic levels were very close to the arsenic limit, but the sulfate levels were 5.6 times higher than the sulfate limit. At a pH of 9, the supernatant was much higher than the accepted pH range of 2-4. By optimizing the complexation process, the arsenic limit might be easily met. The sulfate limit may be more difficult to meet. The pH adjustment to 9 was required to enable the complexation process to work. Options to address the pH would require further evaluation.

The most important limit for this process, even if the supernatant can be made to meet ICPP WAC, is that the precipitated sludge would be significant. In the scenario of two-staged extraction described in Volume I, Section 4.4, the amount of sludge may be 32% of the initial sediment that is extracted (from Volume 1, page 4-4). If 40% of the sediment is extracted (and the remaining 60% is not chemically treated), then the amount of sludge, not including the added ammonium phosphomolybdate, may be

$$\text{Sludge} = 0.32(0.60)(20,700 \text{ yd}^3) = 3,974 \text{ yd}^3.$$

If the scenario suggested in EPA Comment No. 2 is used, then the amount of treated sediment may be as high as 92% of the total, but the sediment dissolution may only be around 10%:

$$\text{Sludge} = 0.10(0.92)(20,700 \text{ yd}^3) = 1,904 \text{ yd}^3.$$

The large amounts of sludge generated to make the extractant meet ICPP waste acceptance criteria would require long-term management. In addition, bin storage for calcined waste at ICPP is very limited. The limited amount of storage for the calcined waste limits the amounts of liquid wastes that ICPP can calcine.

8. *The study presented a conceptual design for a treatment train that would separate out the coarse fraction above mesh 8, acid wash the fines, and treat the extractant. Three alternatives were included for the extractant (ICPP treatment, ion exchange, and chemical precipitation-complexation). Estimated costs for acid washing followed by one of the three extractant options are \$21.2, \$23.5, and \$26.3 million, respectively. Closer examination of the conceptual design and cost estimates in Appendix A, Table 5-3, page 5-8, shows that more than half of the cost for each option is for reagents to treat the extractant. Several of the most significant costs are not adequately backed up by the cost summary and calculations (Appendix A, Attachment L) as listed below:*

- *The cost for the estimated 3,027 gal per day of nitric acid for the soil wash step was not estimated or included in the total cost. This cost should be provided.*
- *The rationale for the NaOH cost of \$3.1 million was not included and should be.*
- *The rationale for the ammonium phosphomolybdate cost of \$15.1 million should be explained.*
- *The calculations for the amount of CS-100 resin required are not clear and cannot be verified. This is a major cost (\$12.4 million). Complete assumptions and calculations should be provided, and regeneration of the CS-100, as suggested in the manufacturer's technical sheet in Appendix A, Attachment G, should be considered to reduce costs and the volume of spent resins for disposal.*
- *The capital cost for the concrete pad with containment is the single largest capital cost (\$.44 million), but is not well supported. The proposed size of 90,000 ft² should be justified, and the reason for doubling the pad cost for "containment" should be explained.*
- *The log washer is another major capital cost item (\$0.34 million), which may not be required, especially if the coarse fraction is acid washed, rather than the fine fraction. This unit should be justified or removed from the treatment train.*
- *The concrete pad for stockpiling WWP sediments is unnecessary if the sediments are stockpiled on the existing ponds. No additional substrate would be contaminated if the soil were stockpiled on top of already-contaminated sediments. Upon completing treatment of the stockpiled soil, the soil under the stockpile could be excavated in the same manner as the rest of the soil. The concrete stockpile pad should be removed from the treatment train.*
- *Several of the operation and maintenance items are based on arbitrary proportions of the capital costs:*
 - *Analytical/monitoring/safety, 20% of capital costs (\$0.62 to \$0.72 million)*

- *Steam/electrical/energy, 25% of capital costs (\$0.77 to \$0.9 million)*
- *Equipment/maintenance, 20% of capital costs (\$0.62 to \$0.72 million)*

These costs should be justified.

Response:

Section 4.4 in Volume I and Section 5 and Attachment L of Volume II have been reviewed and modified by TCT-St. Louis. Each of the bulleted items were addressed. Supporting data, references, and assumptions were provided in the modified sections. In addition, the numbers and calculations were significantly adjusted following a more detailed evaluation. The revised estimated costs were significantly higher than the initial costs that ranged from \$21.2 to \$26.3 million. The preliminary design and cost estimate were prepared within specific limitations or "ground rules." These include the following:

- The most important consideration was that this is a very preliminary design and cost estimate. The design was not intended to include, at this stage, a detailed or especially thorough evaluation of all unit operations. The lesser capital and operating cost items were justifiably less thoroughly evaluated because these items have a smaller impact on the total cost. Even the larger cost items did not include detailed evaluations of individual process design, sizing, energy, manpower and maintenance costs, and other items. The goals of the preliminary design and cost estimate were to (a) design a facility with equipment that would be able to perform the types of physical and chemical unit operations from the treatability, and (b) provide an order-of-magnitude level of estimated costs.
- The scope of the design and cost estimate did not include review and input from architectural and engineering firms or groups, maintenance engineers, plant engineers, or operating engineers, or equipment vendor input.
- The inclusion of various unit operations was based on the expectation in the process design that a certain operation may be required. Alternative unit operations, combining multiple sequences, or other possible cost-saving design features may certainly be justified following a more detailed process design.
- The costs for many capital and operating cost items were based on engineering judgment. Ratios for various costs such as maintenance and energy use are justified because they cannot be better defined without more detailed design information. Rationale and references for such arbitrary estimates have been better documented.
- Estimating the costs for treatment/disposal of secondary waste streams was not within the scope of this preliminary estimate.

A number of editorial changes have been made, in addition to the inclusion of more complete documentation of assumptions, rationale, and references. These edits include the following:

- Typing the calculations in Volume II, Appendix A, Attachments L and M for better legibility.

- Expanding the information and rationale for each of the unit operations listed in Volume II, Appendix A, Section 5.
 - Increasing the font size for print in Figures 5-1 and 5-2, Volume II, Appendix A, Section 5 for better legibility. The basis of Figure 5-2 was changed from a 100-g representative sample to the entire amount of the pond sediments, and included volumes in cubic meters and in drums for the secondary waste streams.
 - More complete footnoting of tables, calculations, etc.
9. *The ICPP WAC for cesium should be determined, and the extractant treatment should be designed to meet that standard.*

Response:

The ICPP WAC does not specify a criterion for cesium. The level of cesium is not important to the processes employed at the ICPP. Concentrations of other contaminants are of critical concern to those processes. In any event, the quantity of dissolved material in the wastes proposed for processing makes this alternative impractical.

10. *The cost estimate should include a table showing mass estimates of the various sludge and resin wastes to result from the proposed treatment. It is not clear whether the net result of the proposed treatment would yield any reduction in volume of solid materials requiring disposal compared to the original soil volume.*

Response:

Table 5-2 in Volume II, Appendix A, Section 5 has been changed for better readability and to include some mass balance information for the treatment process unit operations. Mass and volume data has been added for the input sediment and for the effluent secondary waste streams. The basis was changed from 100 g of representative sediment to the entire estimated amount of pond sediment.

11. *New costs should be estimated using the assumption that the coarse fraction will be treated, potassium nitrate will be used, and the above discrepancies addressed.*

Conclusions and Recommendations

While the report provided much useful data and fulfilled many of its objectives, some of the key conclusions are not adequately supported. As discussed above, the report has not demonstrated that acid washing cannot meet the ROD goal of 690 pCi/g. The study data show that this level can be achieved if acid washing is applied to the coarse fraction. Also, the addition of potassium nitrate to the acid wash process to prevent resorption of the cesium could greatly increase the effectiveness, as suggested by the sequential extraction study. This could also make it possible to treat the soil in a single wash, resulting in less dissolution of the soil matrix.

Response:

Please refer to the response for EPA Comment No. 2. Potassium nitrate was included in the scenario for chemical extraction of the coarse fraction. It was assumed that the addition of potassium

nitrate would enable the chemical extraction efficiency to be 91% for a single stage extraction process. It was also assumed that the sediment dissolution could be reduced to 10% of the extracted material. These assumptions should be considered best case scenario.

Performing a second cost estimate should not be considered necessary, because the mass balance evaluation in the response for EPA Comment No. 2 indicates large amounts of highly contaminated fines and sludge that would require long-term managed disposal. A facility of sufficient size and appropriate design is not readily available.

The costs for such a treatment facility may be qualitatively and quantitatively evaluated by comparison with the preliminary design and cost estimate. The qualitative comparison is discussed in the response for EPA Comment No. 2. Not considered, however, is the potential to eliminate some of the unit operations of the preliminary design. This may be included in a more quantitative comparison.

12. *To support the conceptual design suggested above, additional pilot scale testing of acid washing of the coarse fraction, using potassium nitrate, would be needed. Before this is done, it is recommended that a mass balance be calculated to show the net amounts of soil fractions and sludge residues that require disposal as radioactive, mixed, or hazardous wastes. If it appears that there will be a significant net reduction in volume of such wastes from the original sediment volume, a new conceptual design and cost estimate should be prepared. If no significant net volume reduction can be shown, then the conclusion that soil washing is not feasible will be justified, and further treatability testing of soil washing will not be necessary.*

Response:

Please refer to the response for EPA Comment No. 2.

13. *The conclusion that the cost of the remedial action will exceed the ROD estimate by a factor of 3 is not supported by the cost estimate provided. Many of the units are included in the conceptual design that may not be needed, while some of the major costs are not adequately justified.*

Response:

Please refer to the response for EPA Comment No. 8.